A STUDY OF THE LIQUID-LIQUID EXTRACTION OF BERYLLIUM

With Special Attention Being Given to the System in Which Beryllium Is Separated from Aluminum by the Solvent Extraction of their Thiocyanates

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ROBERT HARRY McCORKELL

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ABSTRACT

The imminent need for supplies of beryllium in greater quantity and purity than the currently used processes for the extraction of beryl can produce, and the existence of large deposits of low-grade, acid-leachable beryllium ores have led to a search for new methods for use in beryllium extractive metallurgy. A promising new process based on the selective solvent extraction of beryllium from aqueous solution is described here.

A consideration of the factors influencing the stability and extractabioity of metal complexes led to the conclusion that the best ligands for the separation of beryllium from other metal ions of inert gas configuration, such as aluminum, by solvent extraction would be easily polarizable monofunctional anions. The thiocyanate ion as its ammonium salt was particularly promising for metallurgical application.

A number of systems, including those using thiocyanate were examined to learn the extent and selectivity of the beryllium extraction given by them and the system using ammonium thiocyanate as the extracting agent and methyl isobutyl ketone as the solvent was selected for special study. The influence of thiocyanate concentration, pH, presence of "inert" salts, metal concentration,

and other factors, on the distribution of beryllium and other metals in this system was studied. The chemical species taking part in the extraction were identified by analysis, spectrophotometry, and the theoretical examination of the influence of various factors (e.g. pH) on the extent of beryllium or aluminum extraction. Data on ore leaching, reagent recovery, and the stripping of the extracts were also obtained, and a tentative flow scheme for the extraction of beryllium from acid leachable bertrandite ores was set up.

Extraction systems using thiocyanate with other solvents have been investigated, some of them extensively, in the same way that the system using methyl isobutyl ketone has. Some of them would no doubt give good separation of beryllium from other metals, but there seems to be no advantage in using them rather than the methyl isobutyl ketone system.

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TABLE OF SYMBOLS AND ABBREVIATIONS

Symbols:

D_X = Distribution coefficient of component X.

$$= \frac{\text{concentration of X in all forms in organic phase}}{\text{concentration of X in all forms in aqueous phase}}$$

q_X = Nernst Constant of species X.

$$= \frac{\text{concentration of species X in organic phase}}{\text{concentration of species X in aqueous phase}}$$

E_X, % ext. of X } Percent extraction of component X

$$V/v = \frac{\text{Volume of organic phase}}{\text{Volume of aqueous phase}}$$

$$\epsilon_x = \frac{\text{Total amount of X in organic phase}}{\text{Total amount of X in aqueous phase}}$$

$$= (V/v)\, D_X$$

ϕ_X = fraction of X left unextracted in aqueous (raffinate) phase.

$D'_X = 1/D_X$

$\epsilon'_x = 1/\epsilon_x$

ϕ'_x = fraction of X left unextracted in organic extract, i.e., in the wash stages

$\beta_{Y/X}$ = The separation factor of Y from X

$= D_Y/D_X$

q/r = The ionic potential of an ion, where q = charge of ion, and r = radius of ion.

K_{fx} = Formation constant of X

[ ] : square brackets: indicate concentration of species enclosed.

M = any metal

M^{+n} any metal ion of oxidation state +n

ABBREVIATIONS FOR SOLVENTS AND REAGENTS

MIK - Methyl isobutyl ketone

1-hex - 1-hexanol

2-oct - 2-octanol

isoam ac - Isoamyl acetate

EtOAc - Ethyl acetate

EtOEt - Diethyl ether

KFR - Karl Fisher Reagent

DEFINITIONS OF TERMS

Extracting Agent - The reagent which reacts with the chemical species to be extracted to form the chemical species which extracts.

Extracting Medium or Solvent - The organic solvent which extracts the extracting chemical species from the aqueous phase.

System or EAtraction System - The aqueous phase, solvent, material to be extracted, extracting agent, and any other reagents added which have a desired effect on the extraction, such as salting out agents or sequestering agents. The term is sometimes used to mean a particular set of reagents and solvents, and sometimes to mean a group of related systems, such as those using a particular extracting agent but different solvents.

Other terms are defined, as they are used here, in the body of the text ("solvent extraction" on page 8 "chemical species" on page 12).

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CHAPTER I

SCOPE AND PURPOSE OF PRESENT INVESTIGATION

The extractive metallurgy of beryllium at present is mainly the processing of beryl, and the two major processes which have been developed for the treatment of this mineral[1] both depend on lengthy batchwise operations with many disadvantages. Heat treatment of the ore is required in both, reagent consumption is high, most reagents are uncrecoverable, and some are moderately expensive (e.g. EDTA). Neither method produces beryllium oxide in a very pure state; in fact further purification is required before it is used in producing the metal[2]. The extension of these processes to other types of beryllium ore would probably not lead to economic production especially if the ore was one of those of lower grade which will have to be used in the future. It is unlikely that either process could be much improved, either as to cost or as to purity of product.

Such processes have sufficed in the past because, until recently, beryllium has been demanded neither in large quantity nor in great purity, and the high grade beryl available could more than supply the demand. Recently, however, beryllium has been finding an amazing number of uses in space and nuclear technology both as the metal and as the ceramic oxide[1,2,3,4,5]. It seems likely that the use of the

element in these fields will continue to increase, for both as the metal and as the oxide it has properties which are in many respects unique, and if the problem of its brittleness is overcome, or if useful alloys of it with other light metals are found, it will probably become the metal of choice wherever lightness must be combined with strength.

These new uses not only increase the demand for beryllium, but, in many cases, call for a metal of purity far greater than either of the present large scale processes can supply.

Increased interest in the development of new processes for the extractive metallurgy of beryllium has resulting not only from the demands of these new uses, but also from the discovery of new types of mineralization extensive and rich enough to be of commercial interest and the imminent necessity of using lower grade ores for which the two current processes are unsuited. Beryl production at present is tied to the very low cost of labour in the regions where it is mined (e.g. the Congo) and to the occurrence of small rich deposits. Most of the world's beryl is not economically mineable because it occurs thinly distributed through a useless matrix and the cost of handling the huge quantities of rock in order to obtain the beryl crystals (either by hand "cobbing" or by the newly developed flotation method) is excessive.

Deposits of non-beryl beryllium ores are presently attracting attention in many parts of the world. Bertrandite is found in huge deposits in the Topaz Mountains of Utah; Chrysoberyl in the Mount Wheeler region of Nevada, and in Alaska. Although these ores have a lower beryllium content than does beryl, the overall deposits in which they occur contain more beryllium than do the overall beryl deposits. While the supply of beryl is definitely limited, the supply of these ores appears to be very extensive.

Thus the nature of these non-beryl ores promises to make them more easily mined and handled than is beryl. Some of them also promise to be more easily extractable, because unlike beryl, they are attacked by sulphuric acid at moderate heat. The availability of some bertrandite ores which are entirely acid leachable prompted the work to be described here.

Many new methods of extracting or purifying beryllium have made their appearance in the literature[6,7,8]. However they are characterised by great expense or no improvement in the purity of the product, and none have yet been shown to be feasible on a large scale.

The present investigation is one of a number undertaken at this laboratory to establish process data useful in meeting the demands described above[9,10,11]. It was intended to develop a process for the separation of beryllium from the other metals, especially aluminum, which co-exist in its ores, by a process of solvent extraction.

Solvent extraction is the term used for liquid-liquid extraction when a species, dissolved in an aqueous solution, is partitioned between that solution and an organic solvent. When used for production or quantitative analysis conditions are maintained such that essentially all of the species enters the organic phase, i.e., it is extracted.

Such a process would begin with the leaching of the ore which would give an aqueous solution containing the beryllium. If, in the leaching and subsequent treatment of the leach, some of the other metals could be left behind the process would be that much improved. Thus, in this study, it was necessary to give some attention to the leaching of ores with the aim of completely removing the beryllium from the ore with as little consumption of reagents and as little coincident leaching of other metals as possible. Chief attention had, however, to be given to finding a suitable solvent extraction system for the selective extraction of beryllium from the solutions obtained by leaching, and to finding the optimum conditions for its use.

Optimizing the process required a knowledge of the way in which the extent of extraction varies with different conditions, e.g., the solvent, pH of the aqueous phase, concentration of extracting agent, etc. This knowledge had to be available both for beryllium and for the other metals which might be in the leach. A brief survey

of these factors for a number of systems permitted the choice of a promising system, which was then more thoroughly examined along the same lines.

The choice of the system also depended on the cost of the reagents used in it, and on the probable ease with which these reagents and the solvent could be recovered for re-use. Also a factor in the choice is the behaviour of the beryllium rich extract in stripping. Reagent recovery and stripping procedures were therefore also investigated.

With the data on factors affecting extraction, reagent needs, costs, and recovery, ore leaching, and procedures as outlined above, it is possible to set up a tentative flow scheme for the separation of beryllium from an ore by solvent extraction using the system chosen. Pilot plant trials can then be carried out, or portions of the process can be tried in the laboratory. An estimate of production costs can be made.

The data on factors affecting extraction can also be used to another end - that of understanding the mechanism of extraction and the nature of the chemical species taking part in it. For example, the way in which extraction varies with the concentration of the ions which react to form the extracted species can be used to obtain the stoichiometry of the extracted species. Since it was desired to understand the extraction in these fundamental terms it was

necessary to make other studies of the system of chief interest - that using ammonium thiocyanate and methyl isobutyl ketone. These included spectrophotometric studies of the extracts, analytic determination of the water extracting with the metal ions, and attempts to isolate the extracted species or to synthesize compounds believed to be related to it.

The research which this thesis describes can then be divided into three main subjects: factors affecting extraction (which includes exploratory work on several systems, but is mainly concerned with the thiocyanate system), chemical species in the extraction, and the development of a flow scheme for the separation of beryllium from its ores.

CHAPTER II

THEORETIC INTRODUCTION

Solvent extraction, and particularly the solvent extraction of inorganic compounds, is one of those fields of chemistry which received great impetus from the advent of nuclear science and technology. The processing of ores for the production of nuclear fuels or of those many formerly little used elements which have recently come into prominence as neutron absorbers, neutron moderators, high temperature ceramics and alloys, etc. depends heavily on solvent extraction, and other radiochemical problems, such as the reprocessing of spent reactor fuels, the recovery and separation of fission products, and the separation of actinides and lanthanides including the transplutonium elements have also seen the use of this technique. In the laboratory, radioactive isotopes are frequently handled by solvent extraction, while the investigation of solvent extraction processes is facilitated immeasurably by the use of radioactive tracers. A great amount of literature has appeared recently which shows the close association of solvent extraction with nuclear science[7,12,13,14] and a symposium on the subject has recently appeared in the journal NUCLEAR SCIENCE AND ENGINEERING[15]. The growth of the two series of reviews on solvent extraction which appear on the analytical[16] and

engineering[17] aspects of the subject testify to its generally increasing importance.

Solvent extraction in other than radiochemical fields is seeing great advances also. The new demands which the utilization of the less familiar elements places on the analyst or chemical engineer are frequently met by solvent extraction techniques and the increasing study of the field has resulted in a great deal of light being thrown on the fundamental chemistry of the phenomena which will be further examined below. The utility of solvent extraction as a tool for the study of aqueous solutions and the equilibria therein has long been known, and its value to these ends will no doubt be greatly increased as further understanding of the processes of distribution is obtained.

As it is used here, the term solvent extraction covers those methods of chemical separation in which a chemical species, initially in an aqueous solution, is extracted from that solution by another liquid, the solvent, which is usually organic and only slightly miscible with water. It is thus one type of liquid - liquid extraction, the type which is usually of most interest to the inorganic chemist. The extraction, except in various types of theoretic studies, is usually desired to be essentially complete, and is intended to separate the species from other materials which extract to a lesser degree.

For convenience, the study of solvent extraction may be considered to take two forms: the study of factors affecting extraction and the study of the chemistry of the process, the chemical species and reactions taking part in it. The first consists as a rule, of nothing but the evaluation of the degree of extraction of the material of interest under varying conditions of temperature, nature of solvent, pH, etc. and is intended to give practical information for the analyst or engineer. But such data usually sheds a good deal of light on the more fundamental problems of the second type (where care is taken to insure the attainment of equilibrium[18]). Obviously study of one of these aspects of a system involves study, and at least partial clarification, of the other. For this reason they will be considered together in the theoretical discussion, although it will be convenient to separate them in the consideration of experimental results.

Before entering upon a consideration of solvent extraction systems and processes however, it will be well to clarify certain points of terminology. The first of these concerns the manner in which the extent of extraction is expressed, and what one is referring to when he states it.

When one is speaking of the distribution of a single chemical species between two solvents which do not enter into any reactions with it (e.g. iodine in the water-carbon tetrachloride system) equilibrium is described by the simple Nernst Law:

$$\frac{m_2}{m_1} = q \ .$$

In this m_2 is the molality of the species in the organic phase, m_1 its molality in the aqueous phase, and q is a constant. In the following, to distinguish this constant from the distribution coefficient, q will be termed the Nernst Constant.

Generally, however, the compound or element of interest exists in more than one chemical form. The measure of extraction wanted and obtained then is not q but D, the distribution coefficient:

$$D_X = \frac{\text{Concentration of X in all forms in organic phase}}{\text{Concentration of X in all forms in aqueous phase}} \ ,$$

q and D could of course be defined as the ratio of concentration in the aqueous phase to that in the organic, i.e., as the reciprocals of the above. This will not be done here however. The reciprocals of q and D, where they are used in this thesis, will be written q' and D'.

q can be expected to be influenced by the following experimental conditions:

(1) The total concentration of the distributing species, insofar as this influences the activity coefficients of that species in either solution,

(2) Those factors which affect the solvent parts of the two solutions, such as the presence of salting out agents, mutual solubility of the solvents, and the concentration of the extracting species, and

(3) Temperature.

This is shown by the thermodynamic expression for the Nernst Constant, which is:

$$q = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-(\phi_2^\circ - \phi_1^\circ)/RT}$$

where γ_1 and γ_2 are the activity coefficients of the extracting species in the aqueous and organic phases respectively, ϕ_1° and ϕ_2° are the chemical potential of the same species in an hypothetical ideal 1 molal solution in the same two solvents, e is the base of natural logarithms, R the gas constant, and T the absolute temperature. This expression is derived in most books on solvent extraction including Morrison and Freiser's[19].

From this expression it can be seen that variations in q with the conditions of the experiment should be small in ordinary conditions, i.e., roughly constant temperature, moderate concentrations of all species, and negligible mutual solubility of the solvents. The distribution of a single species is a simple phenomenon and the Nernst Law is an adequate description of it under any but extreme conditions.

The distribution coefficient of a substance however will be influenced by all the reactions involving the element or compound of interest in both phases and will be a function of all the equilibria existing among the species carrying that compound or ion, or between them and other species in the solution. It will also be a function of the Nernst Constant of all species entering into these equilibria. Cases where D does not vary with experimental conditions will thus be the exception and not the rule. The extent of extraction can still be predicted however, if the particular extraction process is well enough understood and an expression for D in terms of all experimental parameters can be derived. The derivation of such expressions will be further discussed below.

The chemistry of solvent extraction systems is often exceedingly complex. Also the true chemical nature of the materials involved in them is often only vaguely understood, and questions of composition and structure which can in other situations be ignored, such as solvation and ion pairing, take on importance here. Since it is important not to use more exact terminology than is justified one is often forced to use the term "species" or "chemical species" in speaking of the chemistry of solvent extraction systems. These terms mean "atom, ion, molecule, or any aggregrate of these".

Factors Affecting Extraction -- The factors affecting extraction, and their manner and extent of influence, vary with the nature of the extraction system, but some general statements can be made. The most important experimental parameters in an extraction process are:

Temperature. As a rule it is found that the distribution coefficient of a substance decreases as the temperature rises[13,14,21,20]. The reason for this is that temperature has a greater influence on the structure of the aqueous phase than it has on the much looser structure of the organic phase, and the disruption of the liquid structure which progresses with temperature rise has the effect of increasing the solubility of most substances in that liquid. The ratio of solubility in the organic phase to solubility in the aqueous will thus decrease with temperature rise. Cases of increase of distribution coefficients with temperature have been reported however[22] and in these other phenomena, such as endothermic reactions in the formation of the extracting species, predominate.

Solvent. It can generally be said that the extent to which the distribution of a species depends on the choice of the organic solvent is in direct proportion to the extent to which that species takes part in reactions in the extract (organic) phase. The reactions may be of association, dissociation, solvation, etc. Where these do not take place the choice of the solvent will not greatly influence the extent of extraction from the aqueous phase.

Conditions in the Aqueous Phase. This factor will also be important in systems in which the extracted species enters into reactions in the aqueous phase. The conditions of the aqueous phase will influence the extent of these reactions. The presence of salts which do not themselves take part in reactions with the distributing species will, for example, lower the dielectric constant of the aqueous solution thereby permitting greater ion association, and the ionization of chelates,which controls their extraction, is in turn controlled by the pH of the aqueous phase. The distribution of species which do not enter into reactions in the aqueous phase will be governed by conditions in the aqueous phase only insofar as these affect the solvent properties of the water. The addition of an organic liquid to the aqueous phase for example will decrease the extraction of a molecular species such as iodine by providing a solvent in which molecular species are more soluble. The addition of ions which bind water into hydration spheres will drive a molecular solute into the organic phase by decreasing the amount of water available for solvent purposes.

Nature of the Extracted Species and the Extraction Process. This is the most important factor influencing the extent of extraction, and also the factor of most interest in its own right. Solvent extraction systems are classified according to the nature of the chemical species taking part in the extraction. Therefore it will be convenient to consider this subject under the heading of Classification of Solvent Extraction Systems.

Classification of Solvent Extraction Systems. The classification of systems used here is a composite of that used by Morrison and Freiser[19] and that of Diamond and Tuck[23]. It is based on the nature of the chemical species taking part in the extraction, which means that it also arranges systems according to the type of chemical reactions involved in them and the nature of the factors influencing the distribution. Like all classifications it is somewhat arbitrary and limited, but it has proven very useful in arranging and understanding the process of extraction. The chemistry of each group of systems will be described here and the reasons why certain conditions do, or do not, influence the extent of extraction of the extracted species from the aqueous phase examined. Also to be examined is the important matter of developing expressions relating the extent of extraction to all pertinent experimental parameters. Such expressions enable one to predict extraction behaviour in the system and to choose optimum conditions for an extraction or separation of species. They also serve for the detailed description of the system and the extracted species and permit the use of the extraction for the study of a great variety of complexes other than those directly involved in the extraction[16c]. It will become obvious that the developing of such expressions is much easier for some systems than for others. Irving, Rossotti and Williams[24] have however developed a generalized equation for D which

is equally applicable for ion association or pseudo-molecular systems, i.e. for most systems described here. This treatment combines Bjerrum's stepwise equilibria of complexes with the Nernst Distribution Law and includes all possible complications which may occur. Simplified for particular systems, it is useful for evaluating such aspects of the extracted species as the extent of polymerization (of particular value in ion association systems) and the average charge on the metal species in each phase. Work of this nature on ion association systems has been described[25,26,27].

The following is the classification which satisfactorily embraces most solvent extraction systems known today:

(1) Inert Species System. In these systems the material partitioning between the two phases exists in both phases in the same chemical form and the solvents can be considered to act as inert diluents only. All systems in which the extracting species is an organic compound without acid or base groups are included here. So are systems in which the extracting species are halogen molecules, or inert gas atoms. For these systems the simple Nernst Equation is generally very closely obeyed, since the partitioning material exists in a single unreacting form in both phases. Not only can one write:

$$\frac{m_{\text{org. phase}}}{m_{\text{aq. phase}}} = \text{a constant} = q$$

but since this is true at all concentrations up to those at which both phases are saturated we can also predict the constant q from the saturated solubilities of the partitioning material in the two solvents used:

$$q = \frac{\text{saturated solubility in organic phase}}{\text{saturated solubility in aqueous phase}}$$

also the enthalpy change of extraction should be:

$$\Delta H_{\text{ext.}} = \Delta H_{\substack{\text{soln. in} \\ \text{org. phase}}} - \Delta H_{\substack{\text{soln. in} \\ \text{aq. phase}}}$$

Both of these predictions are well confirmed in the case of iodine[16]. Solubilities can be taken as a rough guide in choosing an extracting solvent even where the system is not one of inert species provided the species actually partitioning are recognized and their solubilities are known[19,28].

Qualitatively it can be seen that extraction takes place here because less energy is required to dissolve the molecule or atom in the disordered organic phase than is required to dissolve it in the relatively highly ordered aqueous phase whose structure it must disrupt. Thus for the process

$$(\text{inert species})_{H_2O} \longrightarrow (\text{inert species})_{\text{org. solv.}}$$

$$\Delta F < 0$$

Organic solvents differ little among themselves as to their degree of disorder, and hence the degree of extraction of a given molecule or atom from the aqueous phase will be little affected by the choice of the extracting medium. An increase in temperature will generally decrease q because it will break up the water structure and increase the solubility of the atom or molecule in the aqueous phase without having a corresponding effect on the organic solvent. Salting out agents will increase q by binding the water into hydration spheres about the ions, although interesting cases of decrease of q with the addition of salts are sometimes found. As explained by Diamond[29] this "salting in" occurs when large ions and organic molecules are forced into pairs by the water structure.

(2) Pseudomolecular Systems. In these systems the extracted species is partially ionized in the aqueous phase, but is a molecular compound in the organic solvent. Weak acids and bases are included here, and also the very important metal chelates (where uncharged chelates form).

These are systems in which the material of interest is in more than one chemical form and consequently, although an individual species may obey the Nernst Law, the overall D will vary with those factors which affect the equilibria between the species carrying the material of interest.

If the reactions taking place in a given system are known, an expression for D in terms of the experimental parameters can be derived, and this can be evaluated if the appropriate equilibrium constants are known. Such derivations are probably more successful in predicting extraction behaviour in the pseudomolecular systems than in any other systems involving reactive species. Morrison and Freiser[19] show how, from a few reasonable assumptions about the reactions taking place, a very simple equation for D is obtained for extractions of chelates:

$$D = \frac{K_f \; K_{D_X} \; K_i^{\,n}}{K_{D_R}^{\,n}} \left(\frac{(HR)_o}{(H^+)} \right)^n = K^* \left(\frac{(HR)_o}{(H^+)} \right)^n .$$

Here K_f = cumulative formation constant of chelate

K_{D_X} = Nernst Constant of chelate

K_i = acid ionization constant of chelating agent HR

K_{D_R} = Nernst Constant of chelating agent

$(HR)_o$ = Concentration of chelating agent in organic phase

(H^+) = hydrogen ion concentration in aqueous phase

n = number of chelating groups in metal chelate

A wide variety of predictions concerning the extraction behaviour of chelates can be drawn from this equation[19,28]. Of particular value are the sets of curves showing the extraction of chelates of different K_f as functions of aqueous pH or of $(HR)_o$. These predictions have

been well confirmed for many systems[30,31,32,33,34,35]. This equation can be modified for systems in which the metal ion is involved in reactions of hydrolysis, complexation, etc.[19,30]. Similar equations can be derived for the extraction of weak acids or bases[19,28].

The pseudomolecular systems can be seen to be the simplest systems in which the extracted species is involved in reactions. The reactions are few, and since they are confined to the aqueous phase the choice of solvent will have little effect on the extent of extraction. The reagent concentrations are normally low, hence activity can be approximated by concentration and the mutual solubility of the solvents will not be greatly affected by the presence of the reagents in them.

(3) Ion Association Systems. In these systems the extracted species is formed by the association of species which in aqueous solution normally exist completely dissociated as ions. The ions are capable of extracting as ions (since they are bulky and of low charge density) or are capable of entering solvation reactions with the solvent. In the solvent however they associate at least to some extent, into uncharged ion pairs or higher aggregates. Such ion pairing also tends to make the extracted species more compatible with the organic solvent. The Bjerrum Equation (19, page 31, 36 page 104, 37) shows that ion pairing proceeds to a great extent in solvents whose dielectric constants are in

the region of most liquids used in solvent extraction, and that it can proceed to aggregates higher than pairs.

Ion pairs are more combatible with the organic phase than the aqueous since they are bulky and uncharged. For this reason extraction will be increased by any change which encourages ion pairing in either phase. As the above mentioned equation shows, the extent of ion pairing is inversely proportional to a high power of the dielectric constant of the medium in which the ions exist. Thus extraction will be greatest with solvents of low dielectric constant. Ion pairing in the aqueous phase is encouraged by the lowering of the dielectric constant of the solution by the addition of salts or the dissolving of some of the organic solvent. Too large a solubility of the solvent in the aqueous phase will of course lower extraction by making the extractable species more combatible with the aqueous phase.

The addition of salts to the aqueous phase will also increase extraction of ion association compounds by:

(1) Lowering the activity of the water by binding the water molecules in hydration spheres about the cation of the salt. This leaves less water for solvent purposes and removes water from the hydration spheres of the extracting ions making them less water-like and more extractable. Salts with the most highly hydrated cations will thus make the best salting-out agents,

(2) Providing a greater concentration of the anion for pairing with the extracting metal ion, if the added salt is one of an anion capable of such pairing, and

(3) Increasing ion pairing in the solvent phase if the salt is one of an anion capable of such pairing and also extracts[25].

The extent of ion pairing will also depend on the size and structure of the ions. Small ionic radii favour association (see, however, below) and structures which permit such interactions as hydrogen bonding will also encourage association.

It is obvious from the above that these systems are much more complex than inert species or pseudomolecular systems. The choice of the solvent will for example, play a critical part in deciding the extent of the extraction obtained. Obtaining expressions for D in terms of the experimental parameters is also much more difficult in these systems. There are many reasons for this. In the first place the concentrations of electrolytes used in these systems are as a rule much higher than those used in chelate systems and concentrated solutions of electrolytes present many theoretical problems. In particular activity can no longer be approximated by concentration and small changes in temperature, concentration or other conditions may result in large changes in activity. Also these systems are often characterised by a bewildering array of reactions. The material of interest may exist in several extractable forms

and these may be involved in a reactions in both phases.

Expressions for D in such systems can be obtained in the simpler cases[19]. Also the extensive study of these systems has yielded imperical data from which interesting conclusions can be drawn about the nature of reactions, chemical species, and such taking part in the extractions. The extraction systems of most interest in analysis and industry are included among ion association systems, and although their theoretical treatment is difficult the amount that has been learned about them is impressive.

Ion association systems may be sub-classified, again on the basis of the nature of the chemical species involved. Coördinately Unsolvated Salt Systems. In these systems the extracted species is a salt composed of ions so large that they do not bind water or solvent molecules about them in primary coördination spheres. The lack of hydration of the ions in the aqueous phase has two effects, both favourable to extraction:

(1) Because the hydrogen bonded structure of the water is disrupted by the large ions the water structure may tighten about the ions in a phenomenon similar to that which produces surface tension. This may result in the rejection of the large ions to the solvent phase or in the formation of water structure enforced ion pairing. (Less energy is required for the formation of a single "cavity" for an ion pair than for the formation of two cavities for the two ions). The ion pair will also tend to be rejected to the organic.

(2) No source of energy to remove the water molecules from the hydration sphere of the ions need be found.

These salts may extract either as ions or as ion pairs but in solvents of low dielectric constant they may associate into pairs or larger aggregates. Since such association is favourable to extraction (i.e., because it lowers the activity of the extracted species in the organic phase) the extraction will be somewhat dependent on the nature of the solvent used, particularly on its dielectric constant.

Mineral Acid Systems. These are systems in which the extracting species is a strong acid with a "simple" anion, that is the anion is not a negatively charged complex ion. Such acids are nitric acid, hydrochloric acid, or thiocyanic acid. These are the simplest of the extracting species which extract by virtue of their ability to form some type of solute-solvent complex with the organic solvent molecules. The chief complex here is one of the solvent molecules with the hydrated hydrogen ion. The anion extracts in association with the $H(H_2O)_x(solvent)_y^+$ complex and may, or may not be solvated itself.

This and the following two systems are characterised by strong dependence of the extraction on the properties of the solvent, particularly its basic strength, and the steric

availability of its donor atom. Extraction is also favoured if the solvent is one which is capable of solvating both cation and anion of the extracting species. Because ion association is involved, the nature of the aqueous phase is also critical and the dielectric constant of both phases is important.

These are also the most complex systems. Although much is known about them few general statements about them can be made.

Complex Metal Acid Systems. In these systems the extracting species is a strong acid whose anion is an anionic complex of a metal such as $FeCl_4^-$ or $Co(SCN)_4^=$. Extraction of these acids is essentially the same as extraction of mineral acids. In these systems however there are additional complications arising from the formation of the complex in the aqueous phase in the presence of mineral acids which also extract. This may result in ionic interactions in the organic phase.

Coördinately Solvated Salt Systems. In these the extracted species are salts which extract with coördination of its cation by solvent molecules. The anion of the salt may also be solvated. In many cases the extracted cation is also hydrated with co-extracted water molecules. In the aqueous phase these salts exist as completely dissociated salts except for ion pairing which the presence of high concentrations of electrolytes may bring about.

Here, as in the complex metal acid systems, ionic interactions in the organic phase may result from the co-extraction of electrolytes bearing an anion in common with the extracted metal salt[25].

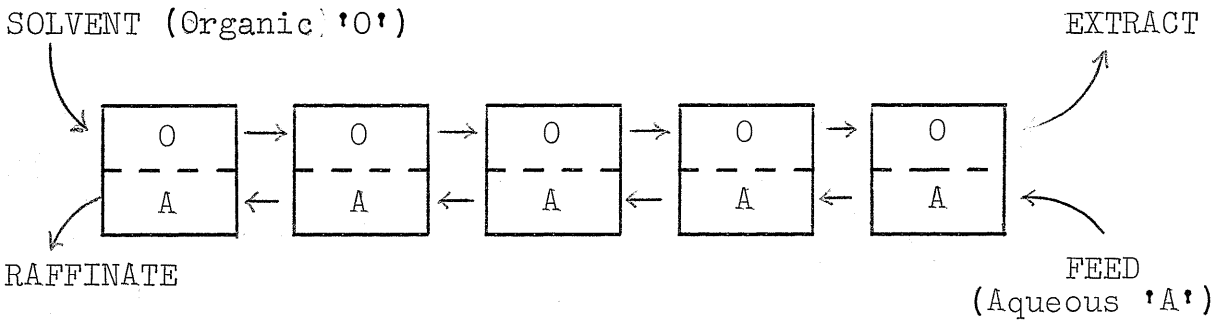
(4) Colloid Systems. In these systems the metal ions are incorporated into salts of high molecular weight which dissolve in the organic solvent in much the same way that soap does in water, that is, by forming colloidal aggregates or micelles, in which the organophilic portions of the salt are turned out into the organic solvent, and the ionic portions are shielded from the solvent in the centre of the micellar structure. It appears that this is the manner in which uranium, molybdenum, and other metals are extracted by high molecular weight amines dissolved in kerosene[14,19].

The above has been a brief discussion of the chemical aspects of solvent extraction. An even briefer discussion of what may be called the engineering aspects follows. This concerns the apparatus, techniques and calculation methods of solvent extraction. These aspects, of course, vary with the manner in which the extraction is carried out. Only countercurrent extraction will be discussed here. Other types of solvent extraction such as those of Craig can be found described in the books by Alders[38], Flagg[12] and Craig[39].

Countercurrent Extraction. This is the method of extraction which makes the greatest use of the solvent, and which, with certain modifications, is capable of achieving at once the greatest extraction and the greatest separation of the extracting materials.

Countercurrent extraction is effected by passing the solvent through the aqueous solution of the materials to be extracted, which is flowing in the opposite direction. Some provision is made to ensure good contact between the two liquids. In industry the most commonly used apparatus for countercurrent contacting of liquids is the centrifugal extractor, although mixer-settlers or columns may be used. Such apparatus, on a smaller scale, may also be used in the laboratory, although a set of separatory funnels is more useful where theoretical studies are being made.

Diagramatically, countercurrent extraction may be represented by a number of chambers in each of which the two liquids are equilibrated before the transfers, indicated by the arrows, are made:



The number of such chambers through which the aqueous and organic liquids pass before leaving the system is termed the number of stages of the extractor. Since equilibrium is achieved in each chamber before either liquid is moved to the next stage, each chamber constitutes a theoretical or ideal stage. The extent of extraction of a material in such an extractor is related to the distribution coefficient of that substance and to the number of theoretical stages in the extractor.

There are several mathematical treatments which relate the extent of extraction in such an apparatus to the number of ideal stages, n, and the distribution coefficient of the extracting species, D_x. Probably the most straightforward and useful is that of Kremser, whose equation is derived by Alders ([38], page 92) and in appendix 1 of this thesis. This equation is

$$\phi = \frac{\epsilon - 1}{\epsilon^{n+1} - 1}$$

where ϕ = fraction of component left unextracted in raffinate

n = number of stages

ϵ = extraction factor of component given by:

$\epsilon = (V/v)D$, V = volume of solvent in each stage

v = volume of aqueous phase in each stage

D = distribution coefficient of component

This equation enables one to calculate the number of stages, n, required to reduce the fraction ϕ of the component in the raffinate to any given value provided the volume ratio is given and the distribution coefficient, D, of the component is known, and is constant over the concentration range in question. Alternately, if one is dealing with an extractor which does not consist of discrete stages such as a column, one can calculate the number of theoretical stages to which the apparatus is equivalent from the fraction of a component of known D left unextracted in the raffinate. The only assumption made in such calculations is the constancy of D. However the value of n found for a column, mixer settler, or other such extractor for one component will not necessarily apply for another component, nor for the same component with a different solvent. It is usually assumed however that for two species extracting out of the same aqueous phase into the same solvent the n of a given apparatus is the same for both.

Variations in D with concentration for a given component, and in n from component to component are thus the two possible sources of discrepancy between extractions and separations predicted on the basis of this equation and those found.

For extraction factors above 1 the equation reduces to

$$\phi = \frac{1}{\epsilon^n}$$

for very high n or ϵ. For extraction factors less than 1 it reduces to

$$\phi = 1 - \epsilon$$

for sufficiently high n or low ϵ. From the last it can be seen that, regardless of the number of stages, the fraction of a component left unextracted will never drop below $1 - \epsilon$ if $\epsilon < 1$, and the smaller ϵ is the fewer the number of stages required for ϕ to approach this value. Thus if a component Y is to be completely extracted from an aqueous solution, and at the same time purified as far as possible from a second component X, and $\epsilon_Y = k\epsilon_X$, $(k < 1)$ (i.e., both extraction factors are increased in the same way by some factor such as solvent ratio) then this is best achieved by setting $\epsilon_Y = 1$. This will insure that all of Y is extracted if sufficient stages are used, while the maximum possible amount of X is left unextracted.

Setting up conditions for the best extraction and separation thus requires a knowledge of the manner in which the distribution coefficients of the components of interest vary with conditions.

As shown, if $\epsilon_Y \geq 1$ there is no limitation to the recovery of Y from the aqueous phase which can be achieved by a sufficient number of stages. However the contamination of the extract by X cannot be reduced below the value given by:

fraction of X extracting with Y = ϵ_X

where ϵ_X is the value of the extraction factor of X in conditions where $\epsilon_Y = 1$, unless a smaller recovery of Y can be accepted.

Two-solvent extraction avoids this limitation on the purity of extract obtainable. In this system the extract stages, which are as pictured above, are followed by a number of "wash stages" in which the extract is equilibrated with a "second solvent". This "second solvent" is usually an aqueous solution of the same composition as that from which X and Y are extracting but lacking X and Y. Obviously, because $D_Y = \frac{(Y)_o}{(Y)_A}$ is greater than $D_X = \frac{(X)_o}{(X)_A}$ this aqueous solution will wash more X than Y out of the extract and the extract will be further purified at every step. It is also obvious that if, in these stages $\epsilon_Y > 1$ and $\epsilon_X < 1$ then $\epsilon'_Y < 1$ and $\epsilon'_X > 1$ so that there is no limitation to the amount of X which can be removed from the extract in these stages while there is a limit to the amount of Y which is washed out. This again assumes that ϵ does not change with the concentration of the species to which it refers. It may be noted however that this assumption is more reasonable in the wash stages than in the extract stages since the concentrations, and particularly the concentration of X, will be smaller. Generally excellent results can be expected from two-solvent extraction.

The aqueous wash from the wash stages is passed into the extract stages with the feed, and hence Y is not lost by this technique even if the amount of it leaving the extract in the wash stages is large.

Appendix 2 shows how Kremser Equation Calculations are applied to two-solvent extraction.

CHAPTER III

STUDY OF FACTORS RELATING TO THE EXTRACTION OF BERYLLIUM AND AFFECTING THE EXTENT OF ITS EXTRACTION

Section I: INTRODUCTION

The study of factors affecting extraction carried out here began with a search for a suitable system for the selective extraction of beryllium from aqueous solution by organic solvents. This was followed by a study of the system chosen, intended to show how the extraction and separation of beryllium could be optimized. As such it is under this heading that most of the data relating to the practical solution of the problem given will be set out and examined. The application of the data will, however, be left to Chapter V.

An obvious factor affecting the solvent extraction of a metal ion is the extraction system chosen for it. It was considered at the outset that an extraction system for beryllium would be one in which coördination of the aquated beryllium ion by ligands bearing two negative charges would displace some or all of the water molecules in the primary hydration sphere and produce an uncharged and less water-like species more compatible with the organic phase than the aqueous.

For the purpose of discussion here, coördinating ligands which might form extractable species with beryllium may be considered to fall into three classes: those which form chelates, those which form complexes with metal ions chiefly as a result of the electrostatic attraction of the cation for the monofunctional anion, (e.g. fluoride, hydroxyl) and those which form complexes in which the polarization of the large monofunctional anion by the central cation is a major factor in the stability. In examining the possible utility of each of these groups of complexing agents in beryllium extraction several matters had to be considered. The first was whether extractable beryllium complexes are likely to result with such a complexing agent. If extractable complexes could be expected it was necessary to decide whether other metals such as aluminum would extract with the beryllium in such a system. Finally there was the question of economics, that is the cost of the reagents per unit of beryllium separated, and their probable recoverability.

Consideration of factors governing the stability of complexes showed that extraction systems using the first two groups of complexing agents would not give selective extraction of beryllium. In order for beryllium to be selectively extracted it must be complexed to a greater extent than the other metals present by a ligand giving extractable complexes, that is, its complex with

the ligand must be more stable than that of the other metals. The chief metal from which separation of beryllium is desired is aluminum. But it has been shown that for a given ligand forming chelate or "electrostatic" complexes the stability of the resulting complexes is proportional to the ionic potential, q/r, of the central cation[40]. In this factor aluminum and beryllium are nearly identical.

$$\frac{q_{Al^{+3}}}{r_{Al^{+3}}} = \frac{3}{0.50A} = 6.0 \qquad \frac{q_{Be^{+2}}}{r_{Be^{+2}}} = \frac{2}{0.31A} = 6.5$$

Extractable beryllium complexes could certainly be expected to form with some of these complexing agents, especially the chelating agents. But aluminum would give equally stable complexes. Stability is not of course the only factor affecting the extractability of a complex, but if the aluminum complex differed from the beryllium complex in this respect it would probably be more extractable because it would be more bulky.

Exceptions to the above statements are found with some chelating agents such as EDTA or 8-quinolinol. With them aluminum forms very stable chelates, but beryllium's chelates show negligible stability. This is presumably due to steric hindrance effects arising from packing the large groups about the small beryllium ion. A separation of beryllium from aluminum can certainly be obtained by using these reagents. This is the basis of the analytical

separation of beryllium from aluminum by precipitating the latter with 8-quinolinol and the selective complexation of aluminum by EDTA is made use of in a method for producing ultrapure beryllium oxide developed by Moore, Shaffer and McDuffie[7]. However systems using chelates were considered unsuitable here because of the high cost of chelating agents.

No case is known in which beryllium forms significantly more stable chelates or complexes of the "electrostatic" type than does aluminum with the same complexing agent. Such differences as there are in stability favour the aluminum complexes[41,42], probably because of steric effects such as described above, and because repulsion between similarly charged groups would be less when they are distributed about the larger aluminum ion than when they are distributed about the beryllium ion.

The third class of complexing agents gave better promise of providing a suitable solvent extraction system for beryllium. The complexing agents which fall into this class are large singly charged anions which form weak complexes with such "inert gas configuration" cations as beryllium and aluminum. Because of their large size and low charge, electrostatic attraction between them and the cation would not be expected to give a very stable complex

but polarization of the anion by the cation would be expected. This phenomenon would account for most of the stability of the resulting complex. The polarizing power of a cation is proportional to the ratio of the charge of that cation to the square of its radius (q/r^2)[43] and in this function beryllium differs considerably from aluminum:

$$(q/r^2)_{Be^{+2}} = 20.8 \qquad (q/r^2)_{Al^{+3}} = 12.0$$

On this basis beryllium could be expected to form considerably more stable complexes with these anions than aluminum. The complexes of both metals would be weak, but this could be offset to some extent by increasing the concentration of the complexing agent. By the correct choice of anion and concentration a state could be reached in the aqueous phase in which a much greater fraction of the beryllium is in the form of an extractable complex than the aluminum.

Thus at least a partial separation of beryllium from aluminum could be achieved by the solvent extraction of such a solution. Interference from those elements which occur about the ends of the transition series would be expected, but since it seems that interference is inevitable this would at least constitute the least objectionable type of interference. These elements generally coexist with beryllium only in small amounts and other

simple chemical techniques exist for their separation from beryllium.

This third class of complexing agents includes such ions as iodide, azide, cyanide, cyanate, thiocyanate and selenocyanate. Most of these could be discarded at the outset as being impractical or too costly. Thiocyanate however is readily available, cheap, stable, and non-toxic. Certain previous work[44] indicated that it is possible to obtain extractions of beryllium using it. It thus appeared to be particularly promising.

Work on thiocyanate, and some of the other similar anions, as extracting agents for beryllium and aluminum is described in section 4 of this chapter. For reasons given in that section certain other systems were also explored. Exploratory work consisted in all cases of measuring the distribution coefficients of beryllium and aluminum in the system at a number of different concentrations of the extracting agent. From these results the possibility of obtaining selective extraction of beryllium in the system could be judged.

It was soon decided to concentrate all work on the thiocyanate system. Distribution coefficients of beryllium and aluminum were determined as functions of the solvent, aqueous thiocyanate concentration, initial and equilibrium pH, metal ion concentration, other cations and salts present, and length of agitation time. Distribution coefficients of other metals of

Distribution coefficients of other metals of possible interest in beryllium extractive metallurgy were also determined as functions of the more important of these parameters and a modification of the simple extraction system was tried. In this part of the work the extraction of the thiocyanate itself (e.g. ammonium thiocyanate or thiocyanic acid) and the stripping of the extract were also examined.

The data on factors affecting extraction were to prove useful in elucidating the problem of the nature of the species extracting in the different systems. They also provide the basis for setting up a tentative flow scheme for the separation of beryllium from its ores, as is done in Chapter V. On the whole the data show the correctness of the conclusions drawn above concerning possible extraction systems.

Section 2: PREVIOUS RELEVANT INVESTIGATIONS

Systems for the extraction of beryllium from aqueous solution with organic solvents have been devised utilizing carboxylic acids[16a,45,46], β-diketones[7,16b,47,48], alkyl esters of phosphoric acid[49], Morin[19] thenoyltrifluoracetone[19] and thiocyanate[19,44]. All of these systems have one characteristic in common; unless a suitable second masking agent is added aluminum extracts with the beryllium in comparable or greater amount, and in many cases other metals such as iron also extract.

The second masking agent which is usually added is EDTA. As has been pointed out, beryllium is distinguished from most complex forming metals in not forming an anionic inextractable complex with EDTA, and hence may be extracted or precipitated in its presence while all other metals remain in the aqueous solution.

EDTA is a moderately expensive reagent, but its cost is not prohibitive in beryllium production if a preliminary separation removes most of the aluminum. This is the system used in the hydroxide process of the Brush Beryllium Co.; most of the aluminum is precipitated out as alum ($NH_4Al(SO_4)_2 \cdot 12H_2O$) from the sulphuric acid leach of the sintered ore before EDTA is added and beryllium hydroxide brought down[1]. Solvent extraction of the beryllium after addition of EDTA might produce a purer product

than precipitation does, but probably the advantages of such a system would not be great.

Although Bock[44] indicates a very high degree of separation of beryllium from aluminum in the extraction of their thiocyanates from aqueous solution with ethyl ether, no further work appears to have been done on this system. Probably this was because 100 percent extraction of beryllium is approached only at thiocyanate concentrations where aluminum extraction is also high. Such a situation would not be disadvantageous in continuous countercurrent extraction such as is used industrially, but it would render the system unsuitable for the batchwise extractions of the analysis laboratory which, until recently, were the only type of interest for beryllium. Also the extractions have to be carried out from acid solutions, which would make EDTA useless as a sequestering agent for aluminum.

Thiocyanate extractions in general have been studied frequently, although a comprehensive study of factors affecting extraction in thiocyanate systems has been made only once[44]. Analytical separations have been made using such systems (e.g. zinc from cadmium[44], cobalt from nickel[50]) and as thiocyanate complexes frequently have strong absorption bands, photometric determination of the metal is frequently combined with the extraction[19,51]. It has been found that in aqueous solution thiocyanate frequently associates with other metal complexes, such as

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$Cr(H_2O)^{+3}$, $Cr(NH_3)_6^{+3}$, and $Co(NH_3)_6^{+2}$ with[52] resulting shifts and intensification of the bands of their absorption spectrum, and such complexes have been both extracted and used in photometric determinations[51,53]. Solvent extraction studies have been made of thiocyanate complexes in order to determine their formation constants[50,54]. However the only studies of the liquid-liquid extraction of beryllium thiocyanate have been those of Bock[44] and those comprising this thesis.

The literature on factors affecting the solvent extraction of inorganic compounds generally has been examined elsewhere (Theoretical Introduction) and will not be further discussed here. The thiocyanates however were expected to extract as coördinately solvated salts, and as such the work of Garwin and Hixson[55] was considered particularly relevant.

Section 3: EXPERIMENTAL

Materials and techniques used in this research varied a good deal. Reagent grade chemicals were used when they were available. When necessary lower grade chemicals were appropriately purified to eliminate the possibility of spurious results due to the presence of impurities. The most important reagents and solvents are listed below with information on their source, purity, or purification.

Beryllium sulphate tetrahydrate - "purified" grade from A. D. Mackay and Co. Stock solutions of this were made up and analyzed by precipitation of the oxide[56] or the double ammonium phosphate[57]. Quantitative dilutions of these solutions were made as required.

Ammonium thiocyanate - Fisher reagent grade. This too was usually handled by making up stock solutions and diluting as required. Ammonium thiocyanate is deliquescent as a solid, and in aqueous solutions of the concentrations here used (1M to 8M) it shows a certain instability, slowly decomposing to sulphur and other products with time. For these reasons solutions were always analyzed by titration with standardized mercury (II) nitrate solution shortly before use. The change of titre of ammonium thiocyanate solutions with time however always turned out to be negligible.

Aluminum sulphate and aluminum nitrate - Fisher reagent grade. Stock solutions were made up, analyzed by precipitation of the oxide, or by EDTA-Zn^{+2} back titration[21] and quantitatively diluted as needed.

Other metal salts were the reagent grade nitrate or sulphate. Their solutions were analyzed by the methods indicated in the Table of Results.

Barium thiocyanate - City Chemical Corp. "pure". Recrystal-- lizations from water removed visible impurities. Solutions for use were then made up and analyzed by titration with standard mercuric nitrate.

Solvents and other reagents used in solvent extractions were:

Kerosene - commercial, unpurified.

Di-n-butyl phosphate - this was a mixture 55 percent in di- and 45 percent in mono-n-butyl phosphate. Its density was 1.03 g/ml. Molarities given are for the di-n-butyl phosphate in kerosene or butyl ether solutions.

Acetic acid - reagent grade.

Propionic acid - "Fisher Certified", b.p. range 140.9°C - 141.8°C.

Butyric acid - Fisher reagent grade, b.p. range 160°C - 165°C.

Hexanoic acid - Fisher "purified".

Octanoic acid - Eastman "practical".

Hexyl mercaptan - Matheson, Coleman and Bell, b.p. range 149.5°C - 151.5°C.

Octyl mercaptan - Matheson, Coleman and Bell, b.p. range 197°C - 199°C.

Chloroform - Fisher reagent grade, or redistilled. In the latter case the fraction from 60°C to 61°C was taken.

Butyl ether - redistilled, 141°C - 142°C.

Methyl isobutyl ketone - redistilled, 114°C - 115°C.

1 - hexanol - redistilled, 115°C - 157°C.

2 - octanol - redistilled, 176°C - 179°C.

Isoamyl acetate - redistilled, 131°C - 136°C*.

Ethyl ether - redistilled, 34.4°C - 34.6°C.

2,4 dimethyl pentanone - redistilled, 123°C - 124°C.

Ethyl acetate - Fisher reagent grade, b.p. range 76.9°C - 77.3°C.

Butyraldehyde - redistilled, 74.2°C - 74.6°C.

* This solvent was Matheson Coleman and Bell, technical grade. It distilled steadily over a temperature range from 124°C to 136°C. The fraction from 131°C to 136°C was taken because it was the largest, and because its temperature range was nearest the boiling point (142.5°C) given in the literature for this liquid.

Stock solutions and reagents used in analysis which should be noted are as follows:

EDTA - Reagent grade disodium ethylenediaminetetra-acetate dihydrate was used to make 0.05 M or 0.10 M solutions which were standardized by titrating accurately measured volumes of standard cadmium or copper solutions. The latter solutions were prepared by dissolving the pure metal in nitric acid. The titration procedures were obtained from Welcher[58].

Mercuric nitrate - A 0.10 N solution of this was prepared from reagent grade mercuric nitrate and standardized by titrating weighed samples of dried reagent grade potassium thiocyanate.

Morin (3,5,7,2,4 - pentahydroxyflavone) - This was reagent grade, the practical grade having been shown in this laboratory to be unsatisfactory.

Zenia (p-nitrabenzene azoörcinol) - This also was reagent grade.

The procedure in the studies of the extraction systems was to agitate the desired volumes of aqueous solution and organic solvent together for the desired length of time in glass stoppered separatory funnels. Analysis was then carried out to determine the degree of extraction. The effect of the length of the agitation time was determined for each system and taken into account where other factors were being investigated.

Analyses were as a rule carried out only on the aqueous solutions, the degree of extraction being determined by analyzing the initial and extracted solutions. Analyses of both phases were however carried out where volume changes occur, where the degree of extraction was small, and in cases where special interest attaches to the composition of the organic phase. Where the organic phase was analyzed this was done by evaporating a sample to dryness on a steam bath, destroying the organic matter with nitric acid, and analyzing the resulting aqueous solution by the usual means.

The procedures used in the analysis are briefly described below. Because a number of analyses methods were used the method is given for each metal in every statement of results. The abbreviation by which the methods are identified in the tables is given in brackets below.

Beryllium, Precipitation as Double Ammonium Phosphate, NH_4BePO_4. Ignition to, and Weighing as, Pyrophosphate $Be_2P_2O_7$ (pyrophosphate). This is the method described by Mellick[57]. It was certainly the most accurate method used, but it was slow and troublesome due to the formation of colloidal or peptizing precipitates and the delicate balance of conditions necessary to obtain a stoichiometric and filterable product. There is reason to believe that the organic material sometimes interfered with obtaining a satisfactory precipitate, possibly by complexing the beryllium (precipitates were sometimes slow

forming) or by surface effects. Still it was the method of choice where uncertainty in the results had to be reduced to about ± 0.5 percent and especially for analyzing beryllium stock solutions.

Beryllium, Photometric (zenia). .This is a photometric method using p-nitrobenzeneazoörcinol ("zenia")[59]. It proved to be precise to about ±5 percent, and to be unaffected by any thiocyanate or solvents present. However iron, calcium, aluminum, and other metals present in sulphuric acid leaches of beryllium ores interfered when present in sufficient amount. The practice in using this method for beryllium analysis was to dilute the sample until the beryllium concentration was about 10^{-3}M, 50 ml of such a solution, after addition of reagents and dilution to 100 ml, giving a convenient optical density at 515 mμ in 10mm. cells. For this reason the interference from these other metals was most serious when dealing with solutions of low beryllium concentration. Therefore, when beryllium concentrations were low and the concentrations of other metals high the morin method was generally used.

Beryllium, Fluorimetry (morin). This is a fluorometric method using 3, 5, 7, 2, 4-pentahydroxyl flavone ("morin")[60]. It proved to have a precision of only about ±10 percent, but it was less subject to interference and more sensitive than the zenia method.

Aluminum, EDTA Titration with Haematoxylin (EDTA). An aliquot of the standard EDTA solution is titrated with a diluted solution of the aluminum sample. The indicator is haematoxylin[58]. Under the prevailing conditions $[Al^{+3}] \simeq 0.01$ M, $[NH_4SCN] \simeq 0.1$ M - 0.5 M, some dissolved solvent present this method was shown to be reliable to about ± 0.5 percent. Where the sample contained only the aluminum salt the mean variation was smaller: about ± 0.2 percent.

Aluminum - EDTA - Back Titration with Zinc (EDTA-Zn). In this method an excess of the standard EDTA solution is added to the aluminum solution, and back-titrated with a standard solution of zinc using Eriochrome Black T as the indicator. The standard zinc solution is prepared by dissolving pure zinc metal in hydrochloric acid. This method permitted the titration of aluminum in the organic phase without prior removal of the solvent and redissolving in nitric acid as described above. Solvent, beryllium, and ammonium thiocyanate do not interfere. This method was reliable to about ± 0.5 percent.

Aluminum, Photometry by Extraction of Oxinate (Oxine). In this method aluminum in the aqueous phase is complexed with 8-quinolinol ("oxine") and extracted with chloroform. The optical density of the extract is taken at 395 m [56, 61, 62]. Standards for this procedure were prepared from a solution of 99.9945 percent pure aluminum (from the National Research Council, Ottawa) dissolved in hydrochloric acid.

Aluminum, Precipitation as Hydrated Oxide, Ignition to, and Weighing as the Oxide (oxide). This is the usual gravimetric procedure for aluminum.

Iron was determined by titration with standard dichromate solution. Manganese, nickel, and magnesium were determined by EDTA titrations using, respectively, Eriochrome Black T, Murexide, and Eriochrome Black T, are indicators. Procedures for these titrations are from Welcher[58].

Lithium was determined by flame photometry.

Thiocyanate was determined by titration with standardized mercuric nitrate solution[63]. For thiocyanate in the aqueous phase this method was very simple and precise, neither the metal ions nor the solvents causing any interference. But, as will be described in chapter IV, the titration of thiocyanate in ketones or alcohols is slow, and gives vague end points. Back titration of an excess of mercuric nitrate added to these aqueous solutions proved to be unsatisfactory for the same reasons. It was found that the best procedure for determining thiocyanate concentration in the organic phases was to extract the thiocyanate with a dilute aqueous sodium hydroxide solution. The aqueous extract is then acidified and its thiocyanate concentration determined in the usual way.

All photometric, fluorometric, or flame photometric measurements were made on a Beckman DU quartz spectrophotometer equipped with fluorometric and flame photometric

attachments. pH adjustments and measurements were made using a conventional glass electrode-calomel pH meter. pH adjustments were made using sulphuric acid and aqueous ammonia of such concentration that the volume changes on adjustment were negligible.

Section 4: RESULTS

The systems investigated were those using the following reagents as extracting agents:

(1) di-n-butyl phosphate,

(2) carboxylic acids,

(3) halide and pseudohalide ions,
especially thiocyanate,

the hope being, in each case, that a selective extraction of beryllium could be obtained. Considerations given earlier in this chapter indicated that it was the last group, halide and pseudohalide ions, which offered the most promise of producing such an extraction of beryllium. Di-n-butyl phosphate however was known to give good extractions and separations of some metals[19, page 147]. It is also a cheap and easily handled reagent. Therefore it was of interest to see if it could be applied to the present problem, in spite of the fact that there was no a priori reason to believe that it would extract beryllium selectively from an aqueous solution containing beryllium and aluminum.

The extraction of beryllium and aluminum salts of butyric acid has been reported[45,46] and it was hoped that, by varying the carboxylic acid and/or its concentration, conditions might be found where beryllium extracts in sufficient amount and with sufficient selectivity to permit its separation from aluminum by countercurrent extraction. Again, no a priori reason existed for expecting such a separation.

Neither the butyl phosphate nor the carboxylic acid system proved capable of giving a separation of beryllium from aluminum which is commercially useful. The data presented however have certain interest in themselves. These will be described here and discussed in the next section.

Di-n-butyl phosphate was used as a solution or suspension in an inert solvent (dibutyl ether or kerosene) to extract the metal ions from an aqueous solution containing nitric acid. This system was characterised by:

(1) Considerable extraction of all metals investigated.

(2) Slow extraction, that is, the extent of extraction increases with the length of time that the phases are agitated together.

(3) A tendency to form soapy, very stable emulsions when the aqueous phase contains iron (III), titanium (IV), or aluminum. This is prevented in the cases of titanium and aluminum by the addition of oxalic acid to the aqueous phase. Oxalic acid did not prevent emulsification in the presence of iron (III) however.

Tables I, II, and III show the data which were obtained on the distribution of beryllium, aluminum, [illegible], and titanium in the butyl phosphate system. The initial aqueous solutions here were 0.05 M in the metal sulphate and 1 M in HNO_3. The molarities of di-n-butyl phosphate are

given for the initial organic phases. This reagent dissolved in di-n-butyl ether but in kerosene above 0.1 M it formed a slow settling suspension which was homogenized before use.

This system did not promise to give a sufficiently selective extraction of beryllium, and therefore no further work on it was undertaken.

Certain details of the procedure used in the extractions utilizing carboxylic acids differ from those used in other extraction systems. Where the acid was acetic, propionic, or butyric the aqueous solution was prepared by adding ammonia to 50.0 ml of 0.40 M beryllium sulphate until beryllium hydroxide was quantitatively precipitated. The desired amount of the acid was then added, the precipitate redissolved, and the solution brought to 100 ml. The same procedure was used where the metal was aluminum. The "carboxylate" concentration given in the table then is the sum of the concentrations of the RCO_2^- ion as acid, beryllium or aluminum carboxylate, and ammonium carboxylate in the initial aqueous solution. Where the acid was hexanoic or octanoic and an aqueous suspension of beryllium or aluminum hydroxide was being extracted the procedure was to add ammonia to a 0.20 M solution of the metal ion in a separatory funnel until the hydroxide was quantitatively precipitated. The acid was then added in a volume approximately equal to that of the aqueous solution and the phases were agitated or let stand until the hydroxide had redissolved. This took periods up to one hour.

When analysis of the aqueous phases in these extractions with hexanoic or octanoic acid revealed no detectable concentration of beryllium or aluminum, analysis of the organic phase and measurement of the phase volumes were dispensed with.

The data on this system are set out in Table IV. Chloroform was used as the solvent because it is a convenient extraction medium, forming the lower layer in extractions of aqueous solutions. It is probable however that another solvent such as benzene or kerosene would have given similar results, this being a pseudomolecular system.

Further work on this system was not justified because it, like the butyl phosphate system, does not give selective beryllium extraction.

Considerations given in the introduction to this chapter indicate that halide and pseudohalide ions might produce species with the beryllium ion which could be selectively extracted from aqueous solutions. The ions which suggest themselves as such extractable-species-formers are iodide and perhaps bromide, azide, cyanide, cyanate, thiocyanate, and selenocyanate. These ions have large electron clouds and large radii, and hence are polarizable.

Cyanide and cyanate however cannot be used in the extraction of beryllium from aqueous solutions because, at any pH where beryllium hydroxide dissolves, cyanic or hydrocyanic acid volatilizes. Selenocyanate could be expected to give about the same results as thiocyanate because its size, and the electronegativity of its component atoms are very similar to those of thiocyanate. It was not investigated because it is difficult to obtain and did not promise to give an economically feasible extraction system.

Similar considerations led to the dropping of the azide ion from this research program, although it too, might have given high selective extraction of beryllium.

The halide ions and thiocyanate seemed worthy of investigation because they meet the a priori criteria for a satisfactory extracting-species-former, and because they are cheap, readily obtainable, stable, and non-toxic. The data of Table V show the extractions obtained with these ions using n-amyl alcohol as the extracting medium.

Thiocyanate appeared to be particularly attractive as an agent for forming an extracting species because it gives high extractions and, as the ammonium salt, it is very cheap, Further work quickly showed that similar extractions and much higher separation factors, D_{Be}/D_{Al}, could be obtained for thiocyanate extractions using many

other solvents. For these reasons work hereafter concentrated on factors affecting extraction in the thiocyanate system.

The first factor investigated in the thiocyanate system was that of the solvent. The distribution coefficients of beryllium and aluminum in the systems 3M aqueous ammonium thiocyanate - solvent are shown in Table VI. These data indicate that extraction of either metal from the aqueous phase decreases as the solvents are changed in the order alcohols > ketones ≥ aldehydes > esters > ethers > mercaptans. Carboxylic acids and hydrocarbons or chlorinated hydrocarbons give no extraction at all. The data also show that in a given group of solvents, such as ketones, the extraction decreases with increasing carbon chain length or the presence of side groups on the chains.

On the basis of Table VI and the criteria set down for in Chapter 1 for a satisfactory extraction system, the solvents methyl isobutyl ketone (MIK), 1-hexanol (1-hex), 2-octanol (2-oct), isoamyl acetate (isoam ac), and ethyl acetate (EtOAc) were chosen for a more extended study. Ethyl ether was also of interest because Bock[44] had reported a very high separation factor D_{Be}/D_{Al} for extraction of the thiocyanates by it. However it proved to be impossible to reproduce some of Bock's values, and in any case ethyl ether would be a poor solvent for industrial use because of its high solubility in water and its high volatility.

This selection of solvents was to be steadily narrowed down as work progressed and the characteristics of extraction with each solvent were recognized.

The possibility that the extent of extraction varied with the length of time that the phases are agitated together was checked at the beginning of this work. Extractions are obviously quite rapid as Table VII shows.

Distribution coefficients of beryllium and aluminum thiocyanates in extractions with these solvents were determined as functions of the aqueous ammonium thiocyanate concentration. Table VIII shows that the beryllium and aluminum extraction increases monotonically with the thiocyanate concentration, but in no case approaches 100 percent extraction very closely. Here, and in every other metal thiocyanate extraction it will be shown that, over at least part of the thiocyanate concentration range, the extent of extraction is related to the thiocyanate concentration by the expression

$$E_{M^{+n}} = k\left[\left(M^{+n}\right)_{\substack{\text{equil.}\\ \text{aq.}}}\right]\left[\left(SCN^{-}\right)^{n}_{\substack{\text{equil.}\\ \text{aq.}}}\right]$$

where k is a constant. This will be discussed more completely in the next chapter.

Tables IXA and IXB show the effect of the pH of the aqueous solution on the extent of extraction of beryllium and aluminum. The pH of the aqueous solution was measured in most cases both before the extraction and after. It is

seen that the shape of the E vs. pH curve is the same for both metals and is unaffected by the change of solvent or ammonium thiocyanate concentration. The extraction vs. pH curve for aluminum could not be traced above a pH of 3 however because of the difficulty of redissolving the aluminum hydroxide formed when ammonia is added.

Table X shows the variation of E_{Be} and E_{Al} with the concentration of the metal ion in the original aqueous solution. It also shows that there is really no variation of E_M with metal concentration; the apparent drop of E_M with increasing (M^{+n}) can be accounted for by the decrease of the aqueous thiocyanate concentration which accompanies the extraction of the metal if it is assumed that beryllium extracts as $Be(SCN)_2$ and aluminum as $Al(SCN)_3$. The"predicted" E_{Be} and E_{Al} in this table are taken from a plot of the percent metal extraction against aqueous thiocyanate concentration, the latter having been corrected for thiocyanate extracted with the metal.

Experiments on the effects of salting-out agents show only a slight increase of E_{Be} with the addition of ammonium nitrate, and a decrease with the addition of ammonium sulphate. This probably indicates ion pairing of the beryllium ion with the nitrate or sulphate ion, which would decrease the formation of the extracted species. Such ion pairing would not be expected to be extensive,but it would probably be enough to lower the extraction of beryllium

thiocyanate since the $Be(H_2O)_4^{+2}$ - SCN^- ion pair in water does not have a high association constant (see Appendix 3).

The concentrations of the nitrate or sulphate ions in these cases were in the range 1M to 5M, and it is probable that no significant pairing of the beryllium ion with these anions takes place when the nitrate or sulphate concentration is in the range of the metal ion concentration. Hence the anion of the metal salt was not thought to be a significant factor in deciding the extent of extraction. However the cation of the thiocyanate salt was shown to exert a powerful effect on the extraction E_{Be} increasing in the order ammonium < potassium < sodium < lithium as Table XI shows.

The extraction of the thiocyanate itself is of interest for several reasons. It offers a means of recovering the thiocyanate from the raffinates after extraction of the beryllium. Knowledge of it proved necessary in dealing with problems arising in continuous countercurrent extraction, and it proved of interest in itself as an indication of the nature of thiocyanic acid and the compounds it forms in extracting.

Extraction of thiocyanate by MIK as a function of the aqueous ammonium thiocyanate concentration and of the metal ion present is shown in Table XI. Table XII shows the extraction of thiocyanate as a function of the initial aqueous pH for several solvents.

Table XII shows that here too the assumption that beryllium extracts as $Be(SCN)_2$ and aluminum as $Al(SCN)_3$ is consistent with the facts.

Table XIII shows that an increase of the extraction of both thiocyanic acid (which is to be expected) and of ammonium thiocyanate occurs with lowering of the aqueous pH.

Two other results concerning thiocyanate extraction are of interest. When a solution 3M in ammonium thiocyanate is made approximately 1M in sulphuric acid and equilibrated with an equal volume of carbon tetrachloride or benzene no detectable amount of thiocyanate leaves the aqueous phase. However extraction of thiocyanate into MIK can be made almost quantitative. When an aqueous solution of ammonium thiocyanate has sulphuric acid added until $(H_2SO_4) = (NH_4SCN)$ and this is equilibrated with three times its volume of MIK, 94 percent of the thiocyanate is extracted. When $(H_2SO_4) = \frac{1}{2}(NH_4SCN)$, 74.5 percent of the thiocyanate extracts into MIK at the same volume ratio.

The extraction of beryllium and aluminum thiocyanates by MIK is always accompanied by a rise in pH. This was at first thought to be due to the co-extraction of thiocyanic acid. Actually it is more probably due to the release of hydroxyl ions from hydroxy complexes of the metals, which occurs when the metals extract. Table XVII shows that very little thiocyanic acid can extract at pH's of 3 or higher.

Such an increase in pH is disadvantageous since beryllium extraction falls off rapidly at pH's above 3. This effect is felt especially in countercurrent systems where the pH rises further in each stage, quickly reaching regions where extraction of beryllium is negligible.

It was decided to combat this effect by conditioning the MIK before use by equilibrating it with an acidified solution of ammonium thiocyanate. The thiocyanic acid thereby added to the solvent would provide a source of acid to combat the hydroxyl released during extraction of the metals. The back-extracting of the thiocyanic acid into the aqueous phase during extraction of the metals would also help to offset the loss of thiocyanate to the organic phase.

In the solvent conditioning process finally settled on (arbitrarily) 10 volumes of methyl isobutyl ketone are equilibrated with 1 volume of acidified aqueous ammonium thiocyanate solution. The latter is prepared by adding 11.2 ml of 1:1 (8.9 M) sulphuric acid to 1 liter of 2 M ammonium thiocyanate. This amount of acid gives the initial aqueous solution a pH of about 1.0. The conditioned MIK was found to have the composition:

$$(HSCN) = 0.0329 \text{ M}$$

$$(H_2SO_4) = 0.0008 \text{ M}$$

Extractions both batchwise and countercurrent to 10 stages have been carried out using this solvent in which the aqueous solution varied widely in composition. The concentration of ammonium thiocyanate in the initial aqueous solution varied in these from 1 M to 3 M, the concentration of aluminum or beryllium from 0.00 M to 0.10 M. The pH of the aqueous phase was never found to vary during the extraction by more than one-tenth of a unit (the initial pH in these extractions was usually 2.9). The pH was also maintained constant within these limits when the aqueous solution being extracted was an ore leach with high concentration of ammonium sulphate, magnesium sulphate, potassium sulphate and ferric sulphate. This solution of thiocyanic acid in MIK apparently releases acid while beryllium thiocyanate extracts in the correct amount to exactly counter the effect of the hydroxyl ions released by the extracting beryllium ions. This is excellent for extraction, since it is at aqueous pH's of about 2.9 that the extraction of the metal thiocyanates from aqueous solution is highest.

Conditioned MIK obtained by this method is obviously far superior to pure MIK as a solvent for the extraction of metal thiocyanates. The values in Tables XIV and XVI show the increased extractions obtained by conditioning the MIK. The use of conditioned MIK would permit great savings of the ammonium thiocyanate used to obtain the extractions, and

would permit the use of countercurrent extractors of any number of stages with no decrease of D_{Be} in the later stages due to pH rise.

The extraction of other metals which may occur in beryllium ores is also shown in Table XIV. Iron is the only metal which appears likely to be troublesome, extracting to an extent comparable to, or greater than, beryllium in both its oxidation states. Manganese, should it be in the ore to a significant extent, would also contaminate the extract to some extent, but it would be removed with the aluminum in two-solvent extraction.

Either the extraction of ferrous iron by conditioned MIK is slow or there is some oxidation of it to the more extractable ferric state occuring during the extraction. This is shown by the fact that, at an initial aqueous concentration of ammonium thiocyanate of 1.00 M, $D_{Fe^{+2}} = 0.166$ in a five minute extraction but $D_{Fe^{+2}} = 0.208$ in a fifteen minute one.

Table XV shows that the distribution coefficient of beryllium is affected little, if at all, by the concentration of the beryllium ion in the aqueous solution. (Error in measuring these low concentrations by the morin method is high; the distribution coefficient being a ratio has twice the probable error of the concentrations measured.) However the distribution coefficient of aluminum rises

sharply with decreasing concentration of the aluminum ion below 5×10^{-3} M.

Table XVI shows the variation of D_{Be} with the pH of the aqueous solution, the solvent being conditioned MIK. It also shows that where the aqueous solution has a pH above 3 the ratio $(Be^{+2}):(SCN^{-})$ in the organic phase is, within experimental error, equal to 2.

Sufficient work was done on stripping the extracts to show that beryllium could be completely removed by washing the organic phase with water. However a small amount of an electroyte would have to be added to the water used in stripping to prevent the formation of emulsions. (An emulsion of MIK in water took about 24 hours to settle, but concentrations of salts in the aqueous phase of as little as 0.1 M causes separation of the phases within one minute.) Washing with base to remove and precipitate the metals would probably be unsatisfactory because the gelatinous precipitates would collect at the interface, increasing handling problems, and wasting solvent.

Tables I to XVII. Explanatory Notes

The following tables show the extent of an extraction (percent extraction E, or distribution coefficient D) of beryllium, aluminum, and in some cases other metals in the butyl phosphate, carboxylic acid, and thiocyanate systems as a function of factors elsewhere noted. The extraction of the thiocyanate ion is also shown.

Unless otherwise stated, the volume ratio in these extractions is unity, the agitation time is 5 minutes, and the concentrations noted (in formula weights per liter) are for the initial solutions. The abbreviations for the analysis methods are explained on pages of introduction.

In headings of tables or columns percent extraction is abbreviated "% ext." and concentrations of components are indicated by writing the symbol for that component in square brackets [ ].

TABLE I

Dependence of percent extraction of beryllium by di-n-butyl phosphate on length of agitation time

initial aqueous solution: 1M HNO_3

0.05 M $BeSO_4$

initial organic solutions: as stated

analysis: beryllium: pyrophosphate

Agitation time: minutes	Percent beryllium extraction by:		
	.1M B.P.* in di-n-butyl ether	.1M B.P.* in kerosene	1M B.P.* in kerosene
2	16.1		
5		17.4	88.0
10	18.0		86.1
15	20.4	16.8	

* Di-n-butyl phosphate

TABLE II

Dependence of percent extraction of beryllium on concentration of di-n-butyl phosphate in initial organic solution

solutions: as for Table I

analysis: beryllium: pyrophosphate

[B.P.*] initial in kerosene	% ext. of Be
0.1	18.6
0.2	50.8
0.4	72.9
0.6	75.3
1.0	88.0

* Di-n-butyl phosphate

TABLE III

Extraction of beryllium, aluminum, and titanium (IV), by di-n-butyl phosphate in the presence of oxalic acid

solutions: as for Table I but aqueous
0.3 M in oxalic acid

analysis: Be: pyrophosphate
Al: as Al_2O_3
Ti: cupferron prec. ignited to oxide[56]

Metal ion	$[B.P.^*]_{initial}$ in kerosene	% ext.
Be^{+2}	1	69.0
Al^{+3}	1	45.5
Ti^{+3}	1	48.6

* Di-n-butyl phosphate

TABLE IV

Extraction of beryllium and aluminum, in the presence of carboxylic acids, by chloroform

initial aqueous solutions: 0.2 M in metal and of carboxylate concentration shown (see page 54 from more information on nature of initial aqueous phases.)

analysis: Be: pyrophosphate

Al: as Al_2O_3

Acid	Carboxylate conc. initial aq.	% Be ext.	% Al ext.
Acetic	5.0	3.3	
Propionic	5.0	21.9	95
Butyric	2.0	87.5	100
"	3.0	92.3	100
"	4.0	91.7	100
"	5.0	94.7	100
Hexanoic*		100	100
Octanoic*		100	100

* Used instead of $CHCl_3$ as organic phase.

TABLE V

Extraction of beryllium and aluminum from aqueous solutions of halide-type ions by n-amyl alcohol

initial aq. solutions: [metal ion] = 0.100 M

pH = 3

[halide salt] = as shown

analysis: Be: pyrophosphate

Al: as Al_2O_3

M(metal ion)	Salt & [salt]. Initial aqueous	% M ext.
Be^{+2}	4M NH_4Cl	0.00
Be^{+2}	4M KBr	1.3
Be^{+2}	4M KI	66.6
Be^{+2}	3M NH_4SCN	81.0
Al^{+3}	3M NH_4SCN	41.2

TABLE VI

Extraction of beryllium and aluminum from aqueous solution initially of $[NH_4SCN]$ = 3M, $[Al(SO_4)_{3/2}]$ or $[BeSO_4]$ = 0.10 M, pH = 3 by a variety of organic solvents.

analysis: Be: pyrophosphate

Al: EDTA

Organic solvent	Distribution Coefficient Al	Be
Alcohols		
Cyclohexanol	3.00	6.70
Isoamyl alcohol	0.67	4.55
n-amyl alcohol	0.70	3.27
1-Hexanol	0.77	2.57
Methyl amyl alcohol	0.15	2.03
1-Octanol	0.51	1.66
2-Octanol	0.09	1.28
2-Ethylhexanol	0.30	0.49
Thioalcohols		
Lauryl mercaptan		0.004
Hexyl mercaptan		0.003
Octyl mercaptan		0.000

continued,

continuation of Table VI

Organic solvent	Distribution Coefficient Al	Be
Ketones		
Methyl isopropyl ketone;		4.87
Methyl isobutyl ketone	0.12	2.38
Acetophenone	0.10	2.37
Methyl n-amyl ketone	0.11	1.63
2,4 Dimethyl pentanone	0.005	0.14
Esters		
Ethyl acetate	0.26	1.27
Isoamyl acetate	0.18	1.22
Amyl acetate	0.01	0.12
2-Ethyl butyl acetate	0.008	0.039
2-Ethyl hexyl acetate	0.000	0.0039
Aldehydes		
Butyraldehyde	0.16	2.50
Butyraldehyde (2M Kerosene solution)	0.08	0.64
Acetaldehyde (4M kerosene solution)		0.51
Paraldehyde		0.24
Paraldehyde (2M kerosene solution)		0.11
Ethers		
Ethyl ether		0.14
Butyl ether	0.00	0.00
Isopropyl ether	0.00	0.00

continued,

continuation of Table VI

Organic solvent	Distribution Coefficient Al	Be
Acids (hexanoic, Octanoic, Oleic)	0.00	0.00
Hydrocarbons, chlorinated hydrocarbons (kerosene, benzene, chloroform, carbon tetrachloride)	0.00	0.00

TABLE VII

Effect of length of agitation time on degree of extraction of beryllium by various solvents from aqueous solutions initially of pH = 3.00, $[NH_4SCN]$ = 3.00, $[BeSO_4]$ = 0.190 M

analysis: Be: pyrophosphate

Solvent	% Be extraction after agitation time: 1 min.	5 min.	15 min.
Methyl isobutyl ketone	72.4	71.0	72.3
1-Hexanol	68.0	72.0	69.0
2-Octanol	60.1	56.0	59.6
2,4 Dimethyl pentanone	12.3	12.3	11.6

TABLE VIII

Extraction of beryllium and aluminum by various solvents as a function of the ammonium thiocyanate concentration in the initial aqueous solution. Initial aqueous pH = 3, initial metal concentrations $[Al(SO_4)_{3/2}] = [BeSO_4] = .1M$. Analysis: Be: pyrophosphate; Al: EDTA.

Extraction as % extraction, E.

Solvent	MIK		1-Hex.		2-Oct.		Isoam. ac.		Ethyl ether		Ethyl acetate	
$[NH_4SCN]$	Be	Al	Be	Al	Be	Al	Be	Al	Be	Al	Be	Al
.5	2.9	0.2	8.0	0.0	2.3	0.0	7.1	0.6	5.8		6.9	
1.0	14.4	1.1	23.6	0.1	10.9	0.0	6.9	1.1	9.2		17.1	
1.5	29.4	1.6	41.8	9.0	21.9	1.0	4.5	.8	6.3		23.3	
2.0	43.2	3.7	52.3	19.3	34.1	1.5	20.1	11.1	5.6		30.5	
2.5	59.3	7.0	64.8	30.8	43.9	4.7	29.6	7.9	9.3		42.9	
3.0	71.0	12.7	72.1	41.2	56.1	10.3	44.1	16.1	12.1		58.7	
4.0	78.8	38.5	83.0	73.0								
5.0	83.1	59.1	88.7	82.8								
6.0	85.1	78.1	91.5	80.6								
7.0	86.6	89.8	94.5	93.6								
7.5	88.0		94.7									

TABLE IXA

Extraction of beryllium by various solvents as a function of the initial and equilibrium pH of the aqueous solution. Aqueous solution $[NH_4SCN]$ = 2.00 M; $[BeSO_4]$ = 0.100 M.

Analysis: Be: pyrophosphate; Extraction as % extraction, E.

pH initial	MIK		1-Hex.		2-Oct.		Isoam. ac.		Ethyl ether	
	Equil pH	E	Equil pH	E	Equil pH	E	Equil pH	E	Equil pH	E
.3				12.0		0.0				
.5		11.6	1.40	20.4	1.30	9.0	1.20	6.8		1.4
.6				21.8		12.6				
1.0	1.90	34.5	1.38	39.7	1.42	24.0	1.50	21.7		4.9
2.0	2.93	45.4	2.60	55.3	2.45	44.0	2.51	29.9		6.4
3.0	3.50	42.3	3.33	54.2	3.13	37.0	3.10	30.8		3.4
4.0	4.30	30.7	4.31	26.3	4.19	18.4	4.01	11.3		4.6
5.0	5.20	1.8	5.21	11.0	4.80	6.0	5.00	1.1		4.5

TABLE IXB

Extraction of aluminum by various solvents as a function of the initial pH of the aqueous solution

aqueous solution: $[NH_4SCN]$ and pH as shown

$[Al(SO_4)_{3/2}]$ = 0.100 M

analysis: Al: EDTA

extraction as % extraction, E

pH initial	MIK 3.5M NH_4SCN	1-Hex 2.5M NH_4SCN	Isoamyl acetate 3.0M NH_4SCN
.5	3.7	2.5	0.0
1.0	12.3	15.6	10.9
2.0	18.3	27.7	15.3
3.0	22.8	28.6	16.1

TABLE X

Extraction of beryllium and aluminum by MIK from aqueous solutions of initial pH = 3.00 and initial $[NH_4SCN]$ = 3.00 as a function of initial aqueous metal concentration

analysis: Be: pyrophosphate

Al: as oxide

extraction as % ext., E

$[Be^{+2}]$ or $[Al^{+3}]$	Be			Al		
	E_{Be}	$[SCN^-]$ at equil	E_{Be} from Tab.8	E_{Al}	$[SCN^-]$ at equil	E_{Al} from Tab.8
0.05	78.0	2.92	75	13.2	2.98	12.9
0.10	71.0	2.86	71	12.7	2.96	12.7
0.20	70.0	2.72	69	12.0	2.93	12.1
0.40	58.0	2.54	59	10.9	2.87	11.3
0.80	50.0	2.20	49	10.1	2.76	9.7
1.00	45.0	2.10	46	9.1	2.73	9.2

TABLE XI

Effect of the Associated cation of the thiocyanate salt on beryllium extraction

aqueous solution; pH = 3.00

$[BeSO_4]$ = 0.100 M

1.5 M in indicated thiocyanate salt

analysis: Be: pyrophosphate

extraction as % ext., E

Solvent	Percent Be extracted from 1.5 M solution of:			
	NH_4SCN	KSCN	NaSCN	LiSCN
Methyl isobutyl ketone	28.3	30.6	34.3	47.8
1-Hexanol	38.7	40.1	48.0	56.4
2-Octanol	21.3	21.5	28.4	33.6
Isoamyl acetate	15.2	18.4	21.3	33.0

TABLE XII

Extraction of thiocyanate ion by methyl isobutyl ketone at pH 3.00

$[NH_4SCN]$	(Metal ion)	Total (SCN^-) ext'd, %	Free SCN^- ext'd, %
1.0		2.0	2.0
2.0		2.2	2.2
3.0		2.1	2.1
4.0		2.2	2.2
1.9	Be^{+2}, 0.100	6.6	3.8
2.0	Be^{+2}, 0.100	7.0	2.7
3.0	Be^{+2}, 0.100	6.8	2.3
4.0	Be^{+2}, 0.1000	5.9	2.0
1.0	Al^{+3}, 0.100	3.2	2.9
2.0	Al^{+3}, 0.100	3.3	2.7
3.0	Al^{+3}, 0.100	3.8	2.5
4.0	Al^{+3}, 0.100	4.6	1.8

TABLE XIII

Extraction of thiocyanate ion by several solvents at varying pH in the presence of 0.100 M beryllium sulphate

pH	Percent SCN^- extracted by:		
	1-Hexanol	2-Octanol	Methyl isobutyl ketone
0.3	51.0	51.4	50.0
0.6	31.7	29.4	40.2
1.0	12.6	3.4	18.4
2.0	6.3	2.8	7.3

TABLE XIV

Extraction of various metals by conditioned MIK as a function of the initial ammonium thiocyanate concentration of the aqueous solution. Aqueous solution - pH = 2.9 - 3.0, [metal ion] = 0.100M. Analysis - as indicated.

$[NH_4SCN]$	Dist. Coeffs. of metals determined by analysis method indicated							
	Al^{+3} (EDTA)	Be^{+2} (Zenia)	Fe^{+2} (dichr.)	Fe^{+2} (dichr.)	Mn^{+2} (EDTA)21	M^{+2} (EDTA)21	Mg^{+2} (EDTA)21	Li^{+} (flame phot.)
0.5	0.0012	0.050	3.86	0.014	0.0008	0.004	0.003	0.007
1.0	0.008	0.24	3.63	0.166	0.023	0.0033	0.001	0.009
1.5	0.030	0.52						
2.0	0.042	1.07	4.39	0.903	0.103	0.0033	0.001	0.016
2.5		1.84						
3.0	0.205	2.98	13.80	2.464	0.244	0.0041	0.002	0.035

TABLE XV

Extraction of beryllium and aluminum by conditioned MIK from aqueous solutions initially pH = 2.9 - 3.0, $[NH_4SCN]$ = 1.59 M as a function of initial aqueous beryllium or aluminum concentration

analysis: Be: morin

Al: oxine

Initial aqueous $[Be^{+2}]$ or $[Al^{+3}]$	D_{Be}	D_{Al}
10^{-1}	.57	.023
5×10^{-2}		.023
10^{-2}	.51	.023
5×10^{-3}		.025
10^{-3}	.61	.035
5×10^{-4}		.057
10^{-4}	.76	.154
5×10^{-5}		
10^{-5}	.74	

TABLE XVI

Distribution of beryllium between conditioned MIK and aqueous solution initially of $[BeSO_4]$ = 0.118 M, $[NH_4SCN]$ = 1.514 M, as a function of initial and equilibrium pH

analysis: Be: morin

pH initial	pH equil.	$[SCN^-]$ equil.		$[Be^{+2}]$ equil.		D_{Be}
		aq.	MIK	aq.	MIK	
1.00	1.79	1.301	.235	.088	.029	.33
1.50	2.22	1.390	.144	.083	.039	.46
2.00	2.50	1.418	.110	.079	.041	.52
2.50	2.77	1.428	.0945	.066	.038	.56
3.00	2.88	1.436	.0907	.080	.043	.54
3.50	3.48	1.448	.0714	.094	.039	.41
4.00	4.00	1.467	.0441	.084	.023	.26
4.50	4.30	1.479	.0281	.104	.014	.13
5.00	4.49	1.486	.0223	.103	.011	.10

TABLE XVII

Extraction of ammonium thiocyanate as a function of pH

Initial aqueous solutions here have $[NH_4SCN]$ = 2.00 M, and the pH shown. Column 3 shows the values of E_{SCN^-} expected if thiocyanate extracts only as thiocyanic acid.

pH initial aqueous	$[H^+]$ initial aqueous	$\left(\frac{[H^+]}{[SCN^-]}\right)_{\text{initial aqueous}}$ X 100 (E_{SCN^-} pred.)	E_{SCN} found (MIK)
0.30	0.501	25	50.0
0.60	0.251	12.5	40.2
1.00	0.100	5.0	13.4
2.00	0.010	2.5	7.3
3.00	0.001	0.05	2.2
4.00	0.0001	0.005	0.00*
5.00	0.00001	0.0005	0.00*

* assumed from fact that $[Be^{+2}]$: $[SCN]$ = 1:2 in extract phases equilibrated with solutions of pH > 3.00. See Table XVI.

Section 5: DISCUSSION

Much of the discussion of these results are reserved for the next chapter, for they are significant to the question of the nature of the chemical species taking part in the extraction. The carboxylic acid and butyl phosphate systems will however be fully examined here and then dismissed. The data for the thiocyanate system will be considered here chiefly as it relates to the practical problem of beryllium extraction.

Table VI shows that the ability of the solvents to extract the thiocyanates from aqueous solutions decreases in the order: alcohols > ketones ≈ aldehydes > esters > ethers > mercaptans, carboxylic acids, hydrocarbons and chlorinated hydrocarbons giving no detectable extraction. There is of course considerable variation of the extracting ability within the groups, which reflects steric and molecular weight effects[64].

The use of alcohols for the extraction of beryllium thiocyanate might seem to be indicated by this. However alcohols tend to be unstable in the presence of thiocyanate. They dissolve in acidic solutions of ammonium thiocyanate and react with thiocyanate dissolved in them (especially during redistillation, the reaction products following the distillate) to produce disagreeably smelling

materials which are probably esters. Instability of extracted thiocyanic acid is a problem even in MIK; it is obvious that alcohols "conditioned" in the way that MIK has been would be even more difficult to use. Also the decomposition products of the alcohols and thiocyanate might tend to accumulate in a cyclicsystem.

Ketones and esters extract beryllium thiocyanate almost as well as do alcohols, and they present none of these problems. Also the separation factor, D_{Be}/D_{Al}, tends to be higher in extraction with ketones or esters than in extractions with alcohols. These considerations justified the choice of methyl isobutyl ketone for the extensive study it has received. It is already a widely used commercial solvent in the extractive metallurgy of uranium[12]. It is cheap, stable, and easily handled, and in the present circumstances it is easily repurified by distillation or by washing with aqueous alkali.

The tables contain many examples of other promising solvents. Some of these were the subject of more extended study, but there seemed to be no advantage in using them instead of MIK.

Equilibrium in these systems is obviously reached within less than one minute of agitation. One reason for this is probably that agitation in a separatory funnel is sufficient to divide these solvents to colloidal proportions. Such rapid equilibration apparently does not take place when drops of solvent are rising through the aqueous phase in a column.

In spite of this fine division of the solvent upon agitation no problem of stable emulsion formation has ever been encountered in the thiocyanate system. Even the most viscous of the solvents used separates from the aqueous phase in less than one minute after agitation is stopped.

Because, at a given concentration of the metal ions, $D_{Be} = k\ (SCN^-)^2$ but $D_{Al} = K(SCN^-)^3$ where K and k are constants, the separation factor, D_{Be}/D_{Al} is inversely proportional to the thiocyanate concentration:

$$\beta_{Be/Al} = \frac{D_{Be}}{D_{Al}} = \frac{k}{K}\,\frac{1}{(SCN^-)} = K'/(SCN^-).$$

Thus, in countercurrent extraction the thiocyanate concentration should be the smallest which, for the volume ratio being used, makes $\epsilon_{Be} > 1$. This will ensure the complete extraction of the beryllium (if sufficient extraction stages are used) with the smallest possible contamination of the extract by aluminum, and, of course, with the minimum consumption of thiocyanate.

Maximum extraction of both beryllium and aluminum thiocyanates is reached when the pH of the aqueous phase is between 2.5 and 3.0. These curves of D or E vs. pH provide interesting information about reactions in the two phases, but it does not appear that separation of beryllium from aluminum can be improved by any adjustment of the pH. Rather the pH should be maintained in the region where maximum extraction is achieved in order to economize on the ammonium thiocyanate needed.

That D_{Be} does not change with metal concentration is a highly fortunate circumstance since it permits the prediction of the distribution to be expected with any change of conditions (even those of a different pH over most of the pH range. See next chapter, section 4) from the initial metal and thiocyanate concentrations and one value of D_{Be}. Aluminum could be dealt with in the same way over the concentration range 5×10^{-3} M to 1 M. Where the concentration of the aluminum ion drops below 5×10^{-3} M the rise in D_{Al} with decreasing concentration of the aluminum would have to be taken into account in the calculations.

Apparently nothing is to be gained by the use of salting out agents except:

(1) Lower solubility of the solvent in the aqueous phase, and

(2) An increase in the separation factor $\beta Be/Al = D_{Be}/D_{Al}$. This is noted in the presence of sulphate, in Chapter V. Sulphate is assumed to complex aluminum to a greater extent than beryllium, increasing the separation factor. It is probable that other weak complexing agents could be found which would produce a greater increase on $\beta Be/Al$ and which might have a similar depressing effect on the extraction of other metals such as iron.

But an increase in the distribution coefficients of the thiocyanates upon addition of large amounts of "inert" salts is not to be expected. At the concentrations of salts which are normally necessary to achieve salting effects (e.g. 5 M to 10 M) the interaction of the beryllium ion with the anion of the salt could be expected to be of the same order of magnitude as its interaction with the thiocyanate. As has been pointed out (page 59) the complexing or ion pairing of the beryllium ion by the anion of the salt would not need to be extensive to exert a depressing effect on the extraction of beryllium thiocyanate. Also, while such ions as nitrate or sulphate are not strong complex formers ion pairs containing nitrate have been noted[65] and the effect of sulphate on the distribution coefficients here noted can only be explained by such pairing.

The "cation effect" is no doubt a type of "salting out" phenomenon - one accomplished without the presence of a competing anion. The smaller cations bind

the water into hydration spheres to a greater extent, decreasing the amount of water available for solvent purposes. This effect has been noted before[23], page 179. It is unlikely that any commercial use can be made of this phenomenon however, because potassium or sodium thiocyanate are several times more costly than ammonium thiocyanate.

It is obvious that a simple means of recovering the thiocyanate from the raffinates would be the acidification of the raffinate with sulphuric acid followed by extraction. The use of sulphuric acid is dictated by economics, but results obtained indicate that the sulphate ion has the effect of binding a considerable part of the added hydrogen ions as HSO_4^- in the aqueous phase. This is shown by the fact (page 61) that only when the sulphuric acid molarity is equal to the molarity of the thiocyanate ion in the solution does extraction of the thiocyanate approach 100 percent. On the other hand, where hydrochloric acid is used for acidifying the hydrogen ions are almost completely extracted as thiocyanic acid. The large amount of sulphate in the raffinates from the extraction of ore leaches would no doubt interfere with the recovery of thiocyante by extraction of thiocyanic acid, although it is probable that countercurrent extraction would make fuller

use of the added hydrogen ions. MIK would be a suitable solvent for the recovery of thiocyanate.

Thiocyanate extracting with the beryllium and other metals would be in considerable amount, since the ore leaches would probably have concentrations of beryllium of 0.5 M to 1 M. This thiocyanate would be removed with the beryllium in the stripping stage and would remain in the aqueous solution after the precipitation of the metals as hydroxides. This solution, perhaps after some concentrating, would be added directly to the incoming ore leach.

It is interesting that while little ammonium thiocyanate extracts from aqueous solutions of pH $\geq$ 3, Table XVII makes it clear that not all the thiocyanate which extracts at lower pH's can be thiocyanic acid. Column 3 of this table shows the value of E_{SCN^-} which would be expected on the assumption that only thiocyanic acid extracts, and column 4 shows the value of E_{SCN} actually found in extractions using MIK.

This table also makes clear that, unless thiocyanic acid is a weak acid, most of the thiocyanate which extracts at higher pH's must also be the ammonium salt. There is no evidence to indicate the proportion of the thiocyanate which extracts as the ammonium salt when sufficient strong acid is added to the aqueous phase to convert all the thiocyanate to thiocyanic acid. Further

discussion of the nature of thiocyanic acid and the thiocyanate-solvent species in the extract is taken up in the next chapter.

The small extraction of thiocyanate at the pH's of useful metal extraction also simplifies predictions of extraction under changed aqueous conditions; only the thiocyanate which extracts with the metals need be considered in the calculations.

The "conditioned" MIK has been discussed in the section on Results. It is probable that the conditioning process would have to be modified in large scale practice. In particular, more thiocyanic acid in the solvent would be needed since the amount of the metals being extracted would be greater. Also a more efficient way of adding thiocyanic acid to the solvent would be channeling some of the thiocyanate-impregnated MIK from the thiocyanate recovery stages to the MIK entering the extract stages. This method would give great flexibility in controlling the concentration of thiocyanic acid in the conditioned solvent.

Butyl Phosphate System. The reactions in the butyl phosphate system have not been extensively investigated here. Since the extraction increases with the agitation time it is obvious that the reaction of the extracting agent with the beryllium ion is slow. This seems reasonable in view of

the fact that di-n-butyl phosphate is only very slightly soluble in water, and hence the reaction can take place only at the interface of the solvents. Slow extraction has been noted under other conditions however[20].

The emulsions probably form due to surface activity of butyl phosphate - metal compound which stabilizes the droplets of organic solvent in the aqueous phase. Oxalic acid was chosen to combat this effect simply because it was known to complex some of the metals in question. However extraction of these metals is high in the presence of oxalic acid, and since their oxalates are not extracted by kerosene the effect of oxalic acid cannot be explained as simply one of sequestering the metal ion. It is possible that butyl phosphate is a better solvent for the oxalates than kerosene, and hence, that the metal oxalates extract into kerosene solutions of butyl phosphate without actual reaction of the metal species with the butyl phosphate. It is also possible that the species extracting in the systems containing oxalic acid is an oxalate complex of the metal with associated butyl phosphate molecules. Hardy, Greenfield, and Scargill[49] report such complexes in alkyl phosphate extraction systems. Such a complex could extract but would not be surface active because it would lack distinctly hydrophobic and hydrophilic ends.

The reason for poor selectivity in this system has already been discussed in general terms (Introduction). The extracting species here is a complex formed by electrostatic attraction, and hence its stability depends mainly on the charge-to-radius ratio of the central cation. Beryllium differs little from aluminum in this, and hence will form the extracting species with the butyl phosphate to about the same extent.

Carboxylic Acid System. The extracting species in the carboxylic acid systems is presumably a salt of the metal and acid which is only partly dissociated in the solvent, and which is perhaps also hydrogen bonded to the excess acid. The feature of these metal species which determines its extractability is the size of the hydrophobic organic part of the salt, and the extent to which this part can surround the metal ion. Because of this extraction would increase with the length of the carbon chain of the acid and to a lesser extent with the oxidation state of the extracting metal since a salt of a trivalent metal carries three carboxylate groups while the salt of a divalent metal carries only two. Extraction might also be expected to decrease somewhat on going to larger cations, since these would have a smaller charge to radius ratio other things being the same, and would be more difficult to surround by the hydropholic part of the salt.

These considerations would not lead one to expect great separation of beryllium from aluminum by the extraction of aqueous solutions of their carboxylates. The hydrophobic organic part of the aluminum salt is only slightly greater than that of the beryllium salt, and the effect of its greater size on its extraction is partly offset by the greater size of the aluminum ion.

This prediction, and that of the effect of the carbon chain length, are in accord with the results shown in table IV. It is doubtful whether the differentiation between beryllium and aluminum shown in this table is sufficient to make this system useful. However, with the addition of EDTA a system utilizing these acids might be superior to that suggested by Moore, Shaffer and McDuffie[7] for the production of ultrapure beryllium oxide, since an acid such as octanoic is much cheaper than acetylacetone.

The results described and discussed in this chapter clearly demonstrate the possibility of achieving a separation of beryllium from aluminum by countercurrent extraction using the thiocyanate system. The best system appears to be one using conditioned methyl isobutyl ketone to extract an aqueous solution of pH 2.5 to 3.0 and thiocyanate concentration in the raffinate of 2.0 M. Calculations and experimental results shown in Chapter V and Appendix 2 show that single solvent extraction would

give beryllium oxide containing about four weight percent aluminum oxide if the initial aqueous solution contains equimolar amounts of the two metals. They also show that a few wash stages in which the extract is equilibrated with 2 M aqueous ammonium thiocyanate of pH 2.5 to 3.0 would remove most of the aluminum.

Although, as stated, the butyl- (or other alkyl-) phosphate or the carboxylic acid systems may have their uses in beryllium purification, and may also be of theoretical interest, they were not further investigated, nor will they be further discussed here. The next two chapters deal with further work on the thiocyanate system.

CHAPTER IV

STUDY OF THE CHEMICAL SPECIES AND BEHAVIOUR OF THE THIOCYANATE EXTRACTION SYSTEM

Section 1: INTRODUCTION

The nature of the extracting species in the carboxylic acid and the butyl phosphate systems has been discussed in the last chapter and will not be further examined here. No studies specifically designed to elucidate the nature of the extracting species or the mechanism and chemistry of the extraction were made on these systems.

This chapter will be concerned with a description and examination of data on the extraction of metal thiocyanates.

Beryllium and aluminum might extract from thiocyanate containing aqueous solutions as the uncharged complex, the coördinately solvated salt, the complex metal acid, or a salt of the complex metal acid. None of these possibilities could be ruled out at the outset. The uncharged complex, as opposed to the ion pair, seemed least likely however, because, when metal ions extract as such, the complex is usually a chelate. A case where an uncharged complex of a metal ion and a simple anion forms and extracts has not come to this author's notice. Those extracting species (such as cobalt chloride[35]) which might,

at first, appear to be such complexes are probably actually coördinately solvated or unsolvated salts. On the other hand Katzin[65] reports that the nitrate ion is taken into the coördination sphere of the cobalt ion in organic solvents.

In the present case thiocyanate, to form an uncharged complex, would have to displace two water or solvent molecules from the coördination sphere of the cation. This would require more energy than the complexation would be likely to provide. Some very approximate values for the association constants of the Be SCN^{+} and Al SCN^{+2} ions obtained in this study (by measuring the decolourization of the ferric thiocyanate complex by beryllium or aluminum ions in aqueous solutions of ionic strength equal to 3) shows that the former is about 10, the latter 1. These values show the weakness of this association. The association of the thiocyanate ion with the hydrated beryllium or aluminum ion is probably of the sort described by Phipps and Plane[52] (See pages 41-42.).

The extraction of such an uncharged complex would probably be characterised by relative independence from the nature of the solvent, although a low dielectric constant, favouring association of unlike charges would no doubt enhance it somewhat. Its extraction, like chelate extractions, would constitute a pseudomolecular system.

Aluminum would extract to a lesser extent than beryllium because, with its lower q/r^2 it would be complexed to a lesser extent.

Numerous cases of metals extracting as the complex metal thiocyanic acid $H_m M(SCN)_{n+m}$ are known[44,50,64]. Thiocyanate behaves here exactly as do the other halide and pseudohalide anions, which form similar extracting species with metal ions[67,68] but the greater size and polarizability of thiocyanate have their effects. As Diamond and Tuck point out[23, page 161] doubly charged anions such as $Co(SCN)_4^{=}$ and $Zn(SCN)_4^{=}$ can extract where the ligand is thiocyanate, but not where it is chloride or bromide

Complex thiocyanate anions of beryllium and aluminum would probably have the structures $Be(SCN)_4^{=}$ and $Al(SCN)_4^{-}$. Such species, if formed would probably be extractable. However the complexation of the hydrated beryllium and aluminum ions by thiocyanate is very weak for reasons given above and there seemed no possibility of its proceeding to such ions. Therefore the extraction of beryllium and aluminum as complex thiocyanic acids also seemed very unlikely.

Thus only the coördinately solvated salts seemed probable forms for the extracted species in the beryllium and aluminum thiocyanate extraction system. In the extraction of these species it is generally assumed that the water molecules in the hydration sphere of the cation

are more or less completely replaced by solvent molecules, but the extraction of hydrated cations, it now appears is, quite common[69,70,71]. The species which extracts is a cation however, and hence solvents which have a sterically available basic atom, a high polarity, and a high dielectric constant will constitute the best extracting media[23,64]. The cations which extract best will also be those which are most readily solvated.

The role of the anion in the extraction of these salts is not simple. If they are small and have a large charge density, and readily form stable complexes with the cation they may result in anionic complexes (e.g. $BeF_4^=$) which do not extract because of their small size and large charge. It has been pointed out that a solvent which readily solvates the cation may prevent the formation of anionic complexes of the cation[64]. Larger anions, which do not complex the cation, probably do not have a very active role in the extraction. The cation extracts because it, or its water of hydration, interacts with the solvent molecules. The anions do not have primary solvation spheres and hence interact to a lesser extent with either phase, and extract easily simply because of their electrostatic attraction for the cation. Indeed large or moderately large singly charged anions can, in this connection, be considered as almost organic entities which fit poorly in the aqueous structure and exist in whatever solvent they

are found simply through their electrostatic attraction for the cation. The result of this, where the cation is also large, is to produce water-structure-enforced ion pairing as Diamond points out[29].

However where the size of the anion is not great the use of a solvent which is capable of solvating that anion will enhance the extraction of the salt, especially since such solvents (e.g. aliphatic alcohols) are also capable of solvating the cation.

If beryllium and aluminum thiocyanates extract as coördinately solvated salts one would then expect extraction to increase as the solvent is changed to increase its basicity or the steric availability of its donor atom, i.e., in the order hydrocarbons or chlorinated hydrocarbons $<$ ethers $<$ esters $<$ acids $<$ ketones $\leq$ aldehydes $<$ alcohols. Alcohols in particular should give good extractions since, as stated, they are capable of solvating both anion and cation[23], page 172. The same order, it is worth noting, prevails in the extraction of complex metal acids, because the solvents which solvate the cations most readily are also the solvents which most readily give "-onium" compounds with the hydronium ion.

It should be noted also that in a given extraction system the nature of the extracted species may change with the conditions of the phase from which it is extracting, and perhaps also with the nature of the extracting medium. An ion which extracts as a complex metal acid at high

acidities may, when the aqueous phase contains less acid but a similar concentration of the complexing anion, extract as a salt[67] or as a salt of the complex acid[50]. It is also possible for a metal which extracts as an uncharged complex of a given coördinating anion to form a negatively charged higher complex at a greater concentration of the complexing agent which then extracts as an acid[35] or as a salt of a second cation[72]. A possible case of the effect of the solvent on the nature of the extracting species occurs in the extraction of iron from thiocyanate solutions; when weakly coördinating ether is used as the solvent iron extracts as the thiocyanate anion which has no primary solvation[44], but when the more strongly complexing solvent n-butyl phosphate is used it extracts as the coördinately solvated salt[51].

More will be said about variations in the thiocyanate species found to extract in the next section. Such variations with conditions of extraction had to be considered in the case of the beryllium and aluminum thiocyanate system, especially as extraction was thought to take place from solutions of widely differing acidities.

Since it was considered most likely that the thiocyanates extract as coördinately solvated salts the possibility of polynucleation or polmerization of these

species had to be taken into account. Such complexes have been reported in a number of places and have been used to explain effects noted in solvent extraction[71]. It was of interest to look for these effects and to test for the presence of such complexes in other ways, especially since it might give information on the nature of the species existing in the aqueous phase. Also thiocyanate offered a special advantage for such a study, the bridging thiocyanate which would appear in such polynuclear species being distinguishable from terminal thiocyanate by the frequency of its stretching modes at about 2100 cm^{-1} in the I.R. absorption spectrum[73]. It is generally found that such polymerization enhances the solubility of the extracted species in whichever phase it takes place[23, 71] i.e., by lowering the activity of the extracted species therein. Thus a study of the data on the effect of the concentration of the extracting metal on the distribution coefficient should reveal such polymerization if it is taking place. Polynucleation in the solid or organic solvent should, as stated, be revealed by the I.R. absorbtion spectrum.

Absorption and Raman spectra can be used in other studies of the extracting species, providing information on bonding and structure[65] and serving for the simple identification of the species if it is one which can be isolated and

studied as a simple compound or ion[35,74,26]. In this case the near infra red proved to contain absorption hands which were of interest in the study of the water of the hydration sphere of the extracted cation.

Data on the manner in which the extent of extraction varies with the concentration of the components of the extracted species (e.g. complexing agent, solvating agent in mixed solvents, etc.) can provide information on the stoichiometry of the extracted species[35,72] and analysis of the extract phase can provide the same information if no species but that of interest extract[44] or if the extraction of other species can be allowed for[73].

Studies of the chemical species involved in this extraction system were undertaken along the lines suggested by these considerations. The system of most interest, that of aluminum sulphate or beryllium sulphate - ammonium thiocyanate - methyl isobutyl ketone, appears to be more than ordinarily complicated, and not all the problems presented by it can be said to be settled. However some fairly definite statements will be developed in the last two sections of this chapter concerning the process of extraction and the chemical species in this system.

Section 2: PREVIOUS RELEVANT INVESTIGATIONS

The only work identifying the extracted species in the solvent extraction of beryllium and aluminum thiocyanates is that of Bock[44]. From the analysis of the extract phases he concludes that it is the neutral salt, $Be(SCN)_2$ or $Al(SCN)_3$, which extracts.

This however could not be said to settle the question of the extracting species in the thiocyanate systems. Many other forms have been noted for the extracting species in the extraction of thiocyanates. Bock found such extracting forms as the ammonium salts of the complex metal thiocyanic acid $NH_4Fe(SCN)_4$, $(NH_4)_2\ Zn(SCN)_4 \cdot 4H_2O$, and $(NH_4)_2\ Co(SCN)_4 \cdot 4H_2O$ and Watkins, Welt, and Diamond[23], page 179 have shown that cobalt can also extract as $Na_2\ Co(SCN)_4$. Cobalt has also been shown to extract as the acid $H_2Co(SCN)_4$, and since it can extract as the neutral chloride[35] it can probably extract as the neutral thiocyanate as does zinc[29]. Iron in particular appears in many forms in extracting with thiocyanate. Bock, as stated, finds it to extract as $NH_4\ Fe(SCN)_4$ while it has also appeared as the neutral thiocyanate in carbon tetrachloride solutions of n-butyl phosphate[51] and as the hexathiocyanate complex $Fe(SCN)_6^{\equiv}$ in extractions with $Ph_3\ MeAs^+$[75]. This latter is perhaps the most highly charged anion known to extract into organic solvents, and shows the effect of the

bulk of the SCN^- ion. For these reasons, as noted in the introduction to this chapter, the possibility that beryllium and aluminum thiocyanates extract in different forms in different circumstances as cobalt does from hydrochoric acid solution[35], had to be considered.

The hydration of the extracting cations has been receiving attention recently [69,70,71,76] and the significance of it in extraction has been recognized in at least one case[26]. Interaction of the solvent with the extracting complex is also possible[21,77] and this had special relevance to the extraction of the anion or anionic species in ion-association systems[55, 23 page 180]. The nature of the extracting species is plainly not settled with the recognition of its stoichiometry in terms of the metal and extracting agent and increasing attention is being given today to such questions of extraction as the nature and structure of the solvent (even where it is an "inert diluent" [14,18,77]) the reactions and species in the aqueous phase, and their difference from those in the organic[65], and the actual association in "ion association" systems[65].

Section 3: EXPERIMENTAL

Most of the reagents and procedures used in the work described in this chapter were described in the chapter on factors affecting extraction (pages 43 - 51). Only those which were not there described will be discussed here.

The Karl Fisher Reagent (KFR) used was a stabilized one liquid type manufactured by the Hartman-Leddon Company of Philadelphia. This was handled in an automatic buret filled by a pressure bulb and protected by drying tubes. Samples to be titrated were contained in long necked flasks into which the buret tip could be inserted during titrations. Titrations were carried out to a visual end point, methylene blue being added to improve the colour change thereat[78]. This was done by adding two drops of the saturated ethanol solution of methylene blue to the empty flask, which was then dried for several hours at 80°C and stoppered until use.

The end point colour change for titrations in MIK was from gold to bronze, and less sharp than in methanol where it was from green to bronze. Titrations in MIK could be reproduced to ±1 percent, those in ethanol to ±0.5 percent.

A standard water-in-methanol solution was used in standardizing the KFR. No more than three hours ever

elapsed between a determination of water content in a sample and a standardization of the KFR.

Titrations in MIK were accompanied by considerable evolution of heat. In these cases the stoppered flask was cooled in running water before the last KFR was added.

Absorption spectra of the extracts in the visible and near infra red were obtained on a Beckman DK quartz spectrophotometer. The infra red absorption spectra were obtained on a Perkin-Elmer Model 21 Infrared Spectrophotometer.

In both the spectrophotometry and the Karl Fisher titrations not more than twenty-four hours were allowed to pass between an extraction and the desired determination on the extract. This was in order to minimize the effects of decomposition in the organic solutions. This decomposition was characterised by a precipitate, which is probably sulphur[64] from decomposition of the extracted thiocyanate. It takes place in some extracts to a greater extent than in others, being in general favoured by high concentrations of the extracted beryllium or aluminum species.

Most spectra on the DK spectrophotometer were obtained at a speed setting of 10 which plots the spectrum from 1000 mμ to 2800 mμ over a length of 16.5 cm. However where only the heights of known peaks were of interest a higher speed setting of 3 was sometimes used.

This plots the same part of the spectrum over a length of chart of 5 cm. The chart paper speed is 1.5 cm./min..

Numerous attempts were made to isolate the extracted species or to synthesize compounds believed to be related to it (e.g. aluminum or beryllium thiocyanate). This work was largely unsuccessful, although some results of interest are given in the next section. The compound isolated from the dried, evaporated MIK extract of the beryllium thiocyanate solution was analyzed by standard means (titration of the thiocyanate with mercuric nitrate solution and ignition of a weighed sample to beryllium oxide, beryllium being the only non-volatile component present). It was also analyzed by thermogravimetry, this being performed by Mr. Menno Heinrichs on the thermobalance of his design[79].

Aqueous solutions of beryllium or aluminum thiocyanate were obtained by mixing solutions of beryllium or aluminum sulphate and barium thiocyanate of known concentration in equivalent amounts and filtering off the precipitate of barium sulphate. Evaporation of these aqueous solutions sometimes yielded an undecomposed clear syrup, but never crystals. Since solid beryllium or aluminum thiocyanate could not be obtained without decomposition samples for infra red spectrometry were obtained as follows: potassium bromide was dissolved in an aqueous solution of the appropriate thiocyanate and the

resulting solutions were evaporated until crystals of potassium bromide were obtained. These were shown to contain substantial amounts of thiocyanate and beryllium or aluminum. After drying under vacuum they were ground with more potassium bromide, pressed into pellets, and their infra red absorbtion spectra obtained.

Obviously exchange may have taken place, and the beryllium or aluminum and the thiocyanate in these crystals may not have been in the form of $Be(SCN)_2$ or $Al(SCN)_3$. However the solutions from which crystallization took place were very concentrated and exceedingly viscous, and it was considered probable that at least some of the thiocyanate would be bound to the beryllium or aluminum, especially if there is indeed a tendency toward polynucleation or polymerization in these salts. Comparison of absorption spectra of these thiocyanates with that of the free thiocyanate ion was obtained by taking the infra red absorption spectrum of potassium thiocyanate in potassium bromide obtained by the same process of co-crystallization.

Section 4: RESULTS

An examination of the results relating the percent extraction E_M of a metal ion M^{+n} from aqueous thiocyanate solution to the concentration of thiocyanate in the aqueous phase at equilibrium reveals the relationship:

$$E_M = k\left[(M^{+n})_{\substack{\text{equil.}\\\text{aq.}}}\right]\left[(SCN^-)_{\substack{\text{equil.}\\\text{aq.}}}\right]^n$$

where k is a constant. This is shown by plotting the product $\left[(M^{+n})_{\substack{\text{equil.}\\\text{aq.}}}\right]\left[(SCN^-)_{\substack{\text{equil.}\\\text{aq.}}}\right]^n$ against E_M, a straight line being obtained. This relation has been shown to hold for all solvents investigated including conditioned methyl isobutyl ketone, in the extraction of the beryllium, aluminum, manganese (II) and iron (II). The results for iron (III) which extracts in large amounts, and lithium which extracts very little, are less definitive. Some typical results are shown in Tables XVIII, XIX, and XX, and Figures 1, 2, and 3.

Thus the metals aluminum, beryllium, manganese (II) and iron II extract from aqueous thiocyanate solutions as $Al(SCN)_3$, $Be(SCN)_2$, $Mn(SCN)_2$, and $Fe(SCN)_2$, that is, such formulae represent the ratio of metal to thiocyanate in the extracted species of these metals.

As tables IXA, IXB, and XVI in chapter III show the extent of extraction of the metal thiocyanates is also a function of the aqueous pH, and this effect is not so easily explained. It was at first thought that the decrease in extraction at pH's below 2.5 was the result of the lowering of the free thiocyanate concentration due to the formation of undissociated thiocyanic acid. This however cannot be the case;thiocyanic acid is a strong acid and hence no lowering of the free thiocyanate results from the addition of hydrogen ions to the aqueous solution. A brief digression here will consider the somewhat contradictory evidence on the nature of thiocyanic acid, and show that there can be little doubt that it is strong.

Thiocyanic acid has been reported to be a moderately weak acid for which log $K_1 = 0.85$ [41], but most treatises on inorganic chemistry call it a strong acid[80]. Gorman and Connel[81] report that when a strong acid (i.e., perchloric acid) is added to a solution of potassium thiocyanate the solution has the pH expected from the assumption that no hydrogen ions are removed from the solution as undissociated thiocyanic acid, i. e. ,

$$pH = -\log(H^+) = -\log(HClO_4)$$

This has been confirmed in this laboratory for other acids and thiocyanate salts. Other data obtained in this study

indicate that thiocyanic acid is strong. If the free thiocyanate concentration in the solutions is calculated at different pH's from Suzuki and Hagisawa's value of $K_{1(HSCN)}$[41] it is found that below a pH of 2.5 E_{Be} decreases with the first power of the thiocyanate concentration. This is inconsistent with the results described above. Further it is found here and elsewhere that thiocyanic acid is extracted from aqueous solutions by solvents capable of forming oxonium compounds (alcohols, ketones, etc.) and much more poorly by hydrocarbons or chlorinated hydrocarbons. This is consistent with thiocyanic acid's being strong. Weak acids are easily extracted by hydrocarbons and other "inert" solvents[23, page 124].

The loss of thiocyanate to the solvent phase at low pH's would lower the extraction of the metal thiocyanates, but values of E_{Be} and E_{Al} predicted at pH's below 2 from the data of Tables VIII and XIII are invariably higher than those found, that is, the loss of thiocyanate to the solvent is not enough to account for the decreased extraction of the metals. Another phenomenon must also be acting to lower the extraction of the metals at low aqueous pH's. This other phenomenon is probably the competition of the extracted thiocyanic acid-solvent species with the extracted beryllium or aluminum for the thiocyanate ion. It will be shown later in the discussion of these data,

that this effect could be powerful enough to lower the extraction of the metals quite considerably.

The decrease in the extraction of the beryllium thiocyanate with increase of pH above 3 finds a ready explanation in the complexing of the beryllium ion by the hydroxyl ion. Indeed, if the equilibrium concentrations of beryllium and thiocyanate ions are calculated at a series of pH's from 0.3 to 5 from the distribution coefficients and the value of $K_{f_{Be\ OH^+}}$ [41] it is found once again that $E_{Be} = k(Be^{+2})(SCN^-)^2$ at pH's where the predominating influence on the extraction is that of the formation of the beryllium hydroxy complex. This is at pH's above 2.5. Below pH = 2, where the thiocyanate extracts in significant amounts, this relation is no longer obeyed. As Table XXI and Figure 4 show, maximum extraction occurs at pH = 2.5, but the product $(Be^{+2}) \times (SCN^-)^2$ reaches a maximum at pH = 1.0.

That beryllium extracts from aqueous thiocyanate solutions as $Be(SCN)_2$ is also indicated by analysis of the MIK extracts. Table XVI of Chapter III shows that when the pH of the equilibrium aqueous phase is above 3.0 the ratio $(Be^{+2}):(SCN^-)$ = 1:2 in the organic phase.

Absorption spectroscopy was used to study the chemical species in this extraction system. Work in the infra red region (2μ to 15μ) was hampered by the high

absorptivities of the solvents. Unidentified decomposition products of thiocyanate which have been reported elsewere[52] similarly interfere with work in the ultraviolet region. But the near infra red region (visible to 2850 mμ) was "open" in all the solvents studied and absorption bands of great interest were found there. It was found that:

(1) Both the beryllium and the aluminum thiocyanate extracted species have absorption bands in this region.

(2) The absorption spectra of the beryllium and aluminum extracted species are similar (i.e. have absorption bands at approximately the same wavelength) but are not identical.

(3) The absorption spectrum of both the beryllium and the aluminum extracted species resemble that of water in the same solvent. It is concluded that the absorption bands of the extracted species here observed actually originate in the water of the hydration sphere of the extracted cation.

(4) The absorption spectrum of water in such solvents as alcohols, ketones, esters, etc. which can extract the metal thiocyanates differs greatly from that of water in such "inert" solvents as chloroform. It also differs greatly from solvent to solvent.

(5) The absorption spectrum of water in an MIK extract containing thiocyanate (whether aluminum or beryllium is also present or not) differs from that of water in the pure solvent.

(6) The absorption peaks of water which is not a part of the beryllium or aluminum extracted species can be distinguished on absorption spectra of the extracts made with the pure solvent as the reference solution. The height of these peaks is indicative of the amount of this "free" water. From them it is concluded that the amount of free water in the beryllium extracts is unaffected by the amount of beryllium thiocyanate in the extract. In the aluminum extract however, the amount of "free" water increases as the concentration of the aluminum increases. It is possible to correlate these facts with the results of the Karl Fisher titrations of the total water content of the extracts.

These facts are shown in the following diagrams and tables. In Figures 5a -10a are shown the absorption spectra of water in a number of solvents. Clearly there is some type of interaction between the solvent and the dissolved water, probably hydrogen bonding between the water and the oxygen atoms of the solvent.

Figures 6b -10b show the absorption spectra of these solvents after they have been equilibrated with an

aqueous solution containing beryllium sulphate and ammonium thiocyanate. The reference solution used in obtaining these spectra is, in all cases a "blank extract" that is, the same solvent equilibrated with an aqueous solution of the same concentration of ammonium thiocyanate and the same pH but containing no beryllium. The spectra are recognizable as those of water in the same solvent, but change considerably from those of water bound only by hydrogen bonding to the solvent. That the water producing this absorption is, in some way, part of the beryllium extracted species is shown by the fact that the height of these peaks (optical density at the maximum) is proportional to the amount of beryllium in the solvent.

Where the reference solution is the pure solvent (Figures 6c to 10c) the peaks common to free water and to the beryllium extracted species are of course higher than where the reference solution is the blank extract. Also in the case of MIK the peaks include one, at 2540 m , which does not appear in the spectrum of water dissolved in pure MIK. This peak also appears in the spectrum of the blank extract vs. the pure solvent. It will also be shown that the molar absorptivities of the different "free water" absorption peaks in the spectra of these thiocyanate containing MIK extracts differ from those of water in pure MIK. These facts must mean that there is interaction between the thiocyanate and the water in the MIK solutions.

Figures 6d and 6e show the absorption spectra of MIK extracts of aluminum thiocyanate. It can be seen that the absorption spectrum of the aluminum extracted species is also due to water incorporated in it. However the water spectrum of the aluminum species is not so much changed from that of "free" water and the spectrum of the extract obtained with the pure solvent as the reference solution shows less clearly the two types of water present.

Quantitative data on these absorption spectra was next sought. This was of interest mainly as proof that these peaks actually represent the absorption of the extracted species, in which the metal ion appears, in spite of the fact that they obviously arise from water. Measurement of these absorption bands might also provide a means of beryllium and aluminum analysis, if the extraction conditions could be duplicated sufficiently closely. This method would be particularly valuable in measuring large amounts of these metals, without the necessity of diluting their solutions. It would also permit simultaneous measurement of both the beryllium and the aluminum.

As expected, the comparison of the peak heights in the spectra of the extracts with those of spectra of MIK solutions of known water content did not afford a direct means of estimating the water/metal ratio in the extracted species. However the spectra did provide information,which, in conjunction with the results of

Karl Fisher titrations of the same extracts revealed the nature of the metal-water species.

Complete quantitative studies on the absorption spectra of beryllium and aluminum thiocyanate extracts were made only for extracts with the solvent MIK.

Table XXII shows the relation of the height of the peaks to the concentration of water in MIK. Table XXIII shows the relation of peak height to beryllium content of a number of extracts of beryllium thiocyanate. Also shown is the height of the peaks at 2540 mμ and 2680 mμ (which belong to the "free water") on spectra obtained with pure MIK as the reference solution. It is seen that although there is considerable variation in the heights of these "free water" peaks no trend in their maximum optical density with beryllium concentration is noted. The erratic variation can at least partly be explained by the instability of these extracts, especially the more concentrated ones. From this relative consistency of the height of the "free water" peaks it can be assumed that the concentration of free water in all these beryllium extracts is roughly the same.

It did not prove possible to obtain the absolute value of the free water concentration of these extracts from the height of the peaks at 2540 mμ and 2680 mμ. The peak at 2540 mμ does not appear in the spectrum of

water in MIK which contains no thiocyanate, and the peak at 2680 mμ gives impossibly high values for the free water concentration when its height is compared with the data of Table XX.

The absorption spectrum of the blank extract also proved useless for obtaining its water concentration; when compared with the data of Table XX every peak on it gives a different value for the water concentration and none of these agree with the water concentration obtained by Karl Fisher titration.

Thus it appears that the "free water" of the extracts is in a different chemical form from that of water in pure MIK. This can only mean some type of association of the water with the thiocyanate.

Table XXIV shows quantitative data on the spectra of aluminum extracts. In these spectra the peak at 2680 mμ arises from the extracted species as well as the "free water", and hence only the peak at 2540 mμ can be used as a measure of free water content. The heights of these in spectra of the extracts obtained with pure MIK as the reference solution are shown. In contrast to the situation in the beryllium extracts, the height of this peak in the spectra of the different solvents indicates an increase in the concentration of the free water as the concentration of aluminum in these extracts increases.

Tables XXIII - XXVI show some quantitative data on the absorption spectra of extracts of beryllium thiocyanate obtained with other solvents. Blank extracts in the same solvent served as reference solutions in obtaining these. Here too the height of the water peaks is proportional to the beryllium concentration in the extracts.

Concentrations of beryllium and aluminum in these extracts were all in cases calculated from previously obtained distribution coefficients.

The absolute total concentrations of water in these extracts were obtained by Karl Fisher titrations, the results being shown in Tables XXIX, and XXX. Plots of total water concentration against beryllium or aluminum concentration are also shown (Figures 11 and 12). If it is assumed that the concentration of water which is not part of the extracting species in these extracts is constant then the slopes of these lines are equal to the hydration numbers of the extracting species. On this assumption these plots show the aluminum species to carry nine water molecules with it, and the beryllium species to be variably hydrated depending on its concentration in the extract.

An interpretation of this rather intricate mass of data is offered in the next section.

Solvation of the anion of an extracting salt has been cited as a condition favourable to extraction, and hence it is not surprising that thiocyanate appears to be very readily solvated, not only by alcohols, but also by ketones and aldehydes, This fact is strikingly seen in attempts to titrate thiocyanate dissolved in solvents with mercuric nitrate. Where the solvent is an ester, ether, hydrocarbon, or chlorinated hydrocarbon the titration can be carried out swiftly to an end point as sharp as when only one phase exists. However, where the solvent is an alcohol or ketone the red iron thiocyanate colour returns upon agitation after every addition of mercuric ion, a titration with continuous agitation to a permanently clear end point taking up to half an hour.

Also striking is the the solubility of some solvents in aqueous ammonium thiocyanate solutions. The extent of this solubility has not been determined exactly, but cyclohexanone is certainly soluble to more than one gram molecular weight per gram molecular weight of thiocyanate in the aqueous solution, and furfuraldehyde is also rendered very soluble in water by thiocyanate. Cyanide and iodide have similar effects in rendering these solvents water soluble, but bromide and chloride have no noticeable effect of this sort.

Attempts to isolate the compound formed by the reaction of the solvent and thiocyanate by evaporation in a flash evaporator have however led to its dissociation into the original salt and solvent.

Numerous attempts were made to isolate the species in which beryllium extracts from aqueous thiocyanate solutions. Only one such attempt led to a definite result. In this an MIK extract of an aqueous solution of beryllium sulphate and ammonium thiocyanate was dried several hours with anhydrous sodium sulphate and evaporated to about one twentieth its initial volume at room temperature under a stream of compressed air. The concentrated solution was then kept at about 0°C for several days. A pale pink crystalline material separated out.

A thermogram of this material obtained by Mr. Menno Heinrichs on his thermobalance[71] showed a plateau at 130°C at which 34.9 percent of the weight had been lost, another plateau at 190°C at which 72.3 percent of the weight had been lost, followed by a gradual weight loss which ceased at about 400°C where 90.5% of the weight had been lost. If the compound is $Be(SCN)_2 \cdot 4H_2O$, the first loss (of water) should amount to 36.6 percent of the weight, and the total loss (ignition to beryllium oxide) should be 87.3 percent.

The thiocyanate content of the compound was also determined by titration with mercuric nitrate, and

the beryllium content by ignition of a weighed sample to the oxide. Water was assumed to make up the difference The composition of the compound, determined by this method is compared below with the composition of the hypothetical compound $Be(SCN)_2 \cdot 4H_2O$.

component	percent found	percent in $Be(SCN)_2 \cdot 4H_2O$
Be	3.6	4.5
SCN	58.1	58.1
H_2O	38.3	36.6

The compound isolated was obviously tetrahydrated beryllium thiocyanate. This leaves little doubt that it is in this form that beryllium extracts from aqueous thiocyanate solutions, although both the hydrated cation and the anion must be solvated by the solvent.

The preparation of aqueous solutions of beryllium and aluminum thiocyanate has been described (Experimental, page 111). A better method of preparing these compounds might have been the fusion of the unsintered metal oxides with ammonium thiocyanate[82].

Concentration of these solutions usually resulted in decomposition and produced syrups of amazing viscosity. It appears that reactions of the following kind take place

(1) $Be(H_2O)_x^{+2} \rightarrow Be(OH)_2 + 2H^+ + (x-2)\ H_2O$

(2) $Be(OH)_2 \rightarrow BeO + H_2O$

(3) $BeO + Be(H_2O)_x^{+2} \rightarrow Be.OBe^{+2} + xH_2O$

(4) $H^+ + SCN^- \rightarrow$ thiocyanate decomposition products, H_2S, NH_3, S, etc.

Reaction 3, continuing to considerable polymerization, would lead to the viscous solutions noted. Such viscous solutions have been noted in this laboratory when beryllium oxide is dissolved in beryllium sulphate solutions. Formation of polynuclear $(Be(SCN)_2)_x$ species might also account for the viscosity.

The products of reaction 4, hydrogen sulphide and ammonia, were noted in varying amounts by their smell. Sulphur was always produced in large amounts.

Aluminum thiocyanate was found to be unstable in a manner similar to beryllium thiocyanate.

Both beryllium thiocyanate and aluminum thiocyanate solutions have been evaporated in a flash evaporator without decomposition. The concentrated solutions are always extremely viscous. A glass of aluminum thiocyanate was obtained on one occasion, with some decomposition.

Infra red absorption spectra of beryllium, aluminum, and potassium thiocyanate in potassium bromide

pellets were obtained as described in the Experimental section (page 111). The significant portions of these spectra are compared in figure 13.

Tables XVIII to XXX, and Figures 1 to 13: Explanatory Notes

These tables present data or calculations utilized in the investigation of the chemical species taking part in the thiocyanate extraction system. Figures 1 to 4, 11, and 12 present in graphical form the data of the tables preceding them. Figures 5 to 10 show absorption spectra of extracts of beryllium or aluminum thiocyanate in organic solvents, or absorption spectra of water in the same solvents. Figure 13 shows the infra-red absorption spectra of solid thiocyanates.

The conventions and symbols used in these figures and tables are the same as noted elsewhere (page 66)

TABLE XVIII

Relation of E_{Be} to aqueous thiocyanate concentration

Solvent: 1-hexanol

$(SCN^-)_{aq.}$	$(Be^{+2})_{aq.}$ equil	$(SCN^-)^2_{aq.}$	$(Be^{+2})_{eq}(SCN^-)^2_{aq.}$	E_{Be}
.5	0.092	.25	0.0230	8.0
1.0	0.076	1.00	0.0760	23.6
1.5	0.058	2.25	0.1505	41.8
2.0	0.048	4.00	0.1920	52.3
2.5	0.035	6.25	0.2188	64.8
3.0	0.028	9.00	0.2520	72.1
4.0	0.017	16.00	0.272	83.0
5.0	0.011	25.00	0.275	88.7
6.0	0.008	36.00	0.288	91.5
7.0	0.005	49.00	0.245	94.5

Fig. 1

Extraction of Beryllium Thiocyanate into 1-Hexanol
The product $(Be^{+2})(SCN^{-})^{2}$, where the concentrations are those in the aqueous phase at equilibrium, is plotted against E_{Be}. See Table XVIII.

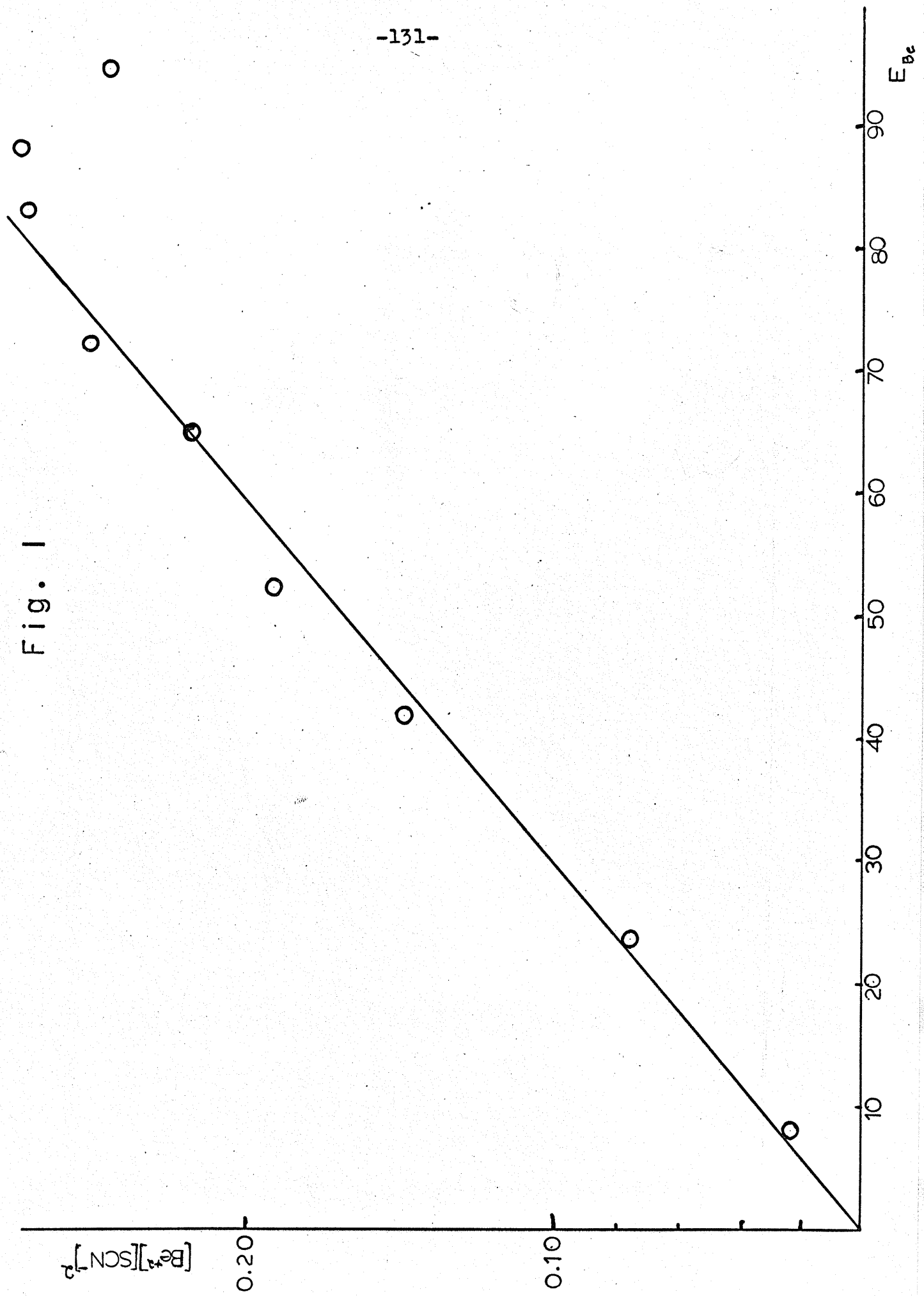


Fig. 1

TABLE XIX

Relation of E_{Al} to aqueous thiocyanate concentration

Solvent: 1-hexanol

(SCN^-)	$(SCN^-)^3_{aq.}$	$(Al^{+3})_{aq.\ equil.}$	$(Al^{+3})(SCN^-)^3_{aq}$	E_{Al}
0.5	.125	0.100	0.0125	0.0
1.0	1.000	0.100	0.1000	0.1
1.5	3.375	0.091	0.3070	9.0
2.0	8.000	0.081	0.648	19.3
2.5	15.625	0.069	1.076	30.8
3.0	27.000	0.59	1.593	41.2

Fig. 2

Extraction of Aluminum Thiocyanate into 1-Hexanol

The product $[Al^{+3}]\,[SCN^{-}]^{3}$, where the concentrations are those in the aqueous phase at equilibrium, is plotted against E_{Al}. See Table XIX.

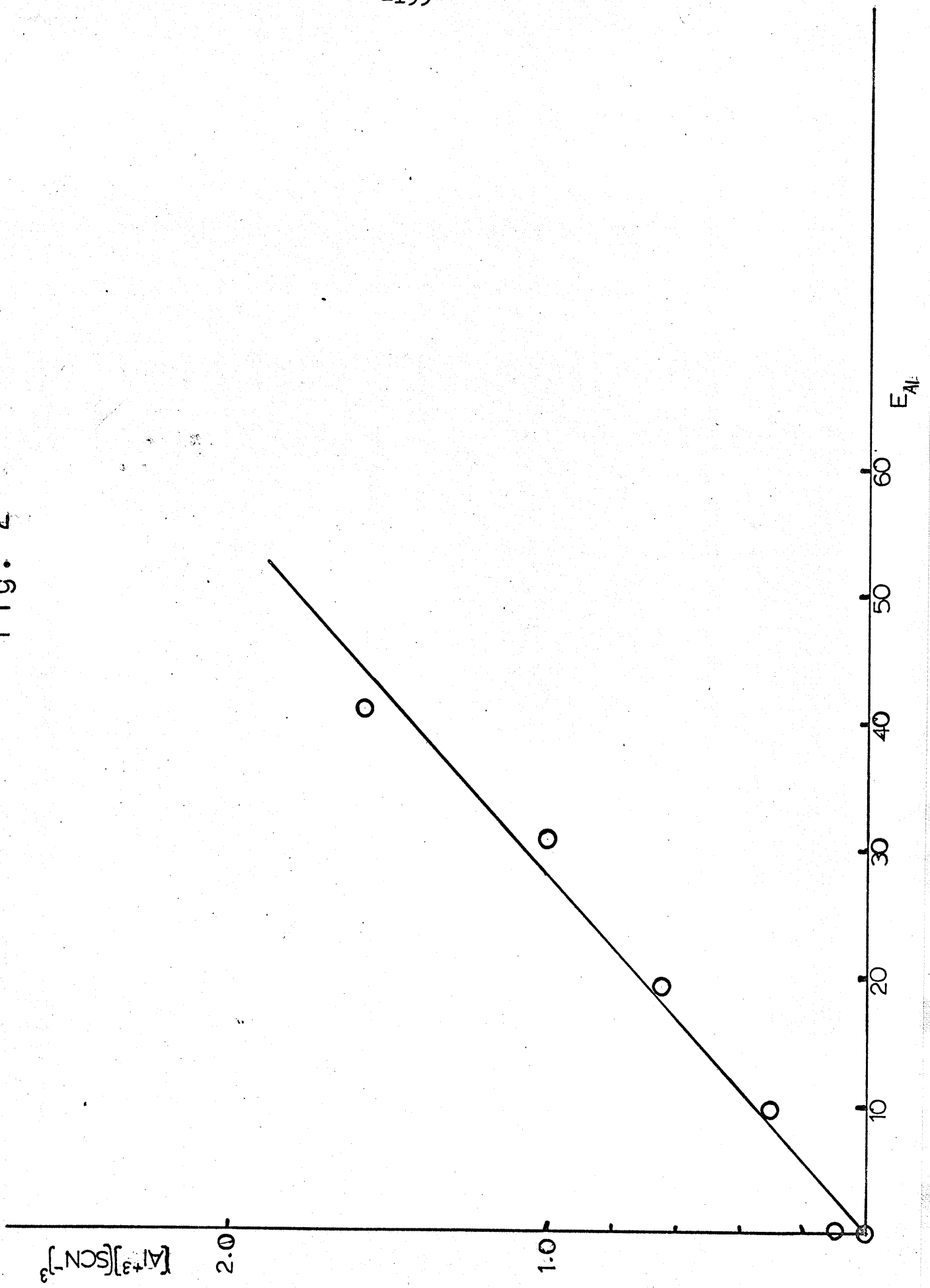


Fig. 2

TABLE XX

Relation of E_M to aqueous thiocyanate concentration for beryllium, aluminum, manganese (11) iron (II) iron (III), and lithium

Solvent: conditioned M1K

(SCN^-)		0.5	1.0	1.5	2.0	2.5	3.0
$(SCN^-)^2$		0.25	1.00	2.25	4.00	6.25	9.00
$(SCN^-)^3$		0.125	1.00	3.38	8.00	15.6	27.0
(M^{+n}) equil.	Be^{+2}	0.094	0.080	0.064	0.045	0.033	0.023
	Al^{+3}	0.100	0.100	0.098	0.096	0.091	0.083
	Mn^{+2}	0.100	0.098	0.094	0.091	0.085	0.080
	Fe^{+2}	0.099	0.086	0.068	0.052	0.038	0.029
	Fe^{+3}	0.021	0.021	0.019	0.016	0.011	0.007
	Li^+	0.100	0.099	0.099	0.098	0.098	0.097
$(M^{+n})_{aq.} X (SCN^-)^n$	Be^{+2}	0.024	0.080	0.144	0.180	0.206	0.207
	Al^{+3}	0.013	0.100	0.330	0.768	1.44	2.24
	Mn^{+2}	0.025	0.098	0.211	0.364	0.531	0.720
	Fe^{+2}	0.025	0.086	0.153	0.208	0.238	0.261
	Fe^{+3}	0.0026	0.021	0.064	0.128	0.156	0.189
	Li^+	0.05	0.099	0.150	0.196	0.245	0.290
E_M	Be^{+2}	5.6	20.0	36.5	55.3	0.290	77.6
	Al^{+3}	0.12	0.80	2.0	4.0	9.1	16.7
	Mn^{+2}	0.08	2.2	5.7	9.3	14.9	19.7
	Fe^{+2}	1.34	14.2	32.0	47.5	61.5	71.1
	Fe^{+3}	79.0	79.2	80.9	84.1	89.0	93.1
	Li^+	0.7	0.9	1.2	1.6	2.5	3.4

Fig. 3

Extraction of Different Metal Thiocyanates into Conditioned MIK

The product $(M^{+n})(SCN^{-})^{n}$, where the concentrations are those in the aqueous phase at equilibrium, is plotted against E_{M}. Different scales are used for the different metals because the values of $(M^{+n}) \times (SCN^{-})^{n}$ and E_{M} vary widely with the metal M. See table XX.

Fig. 3

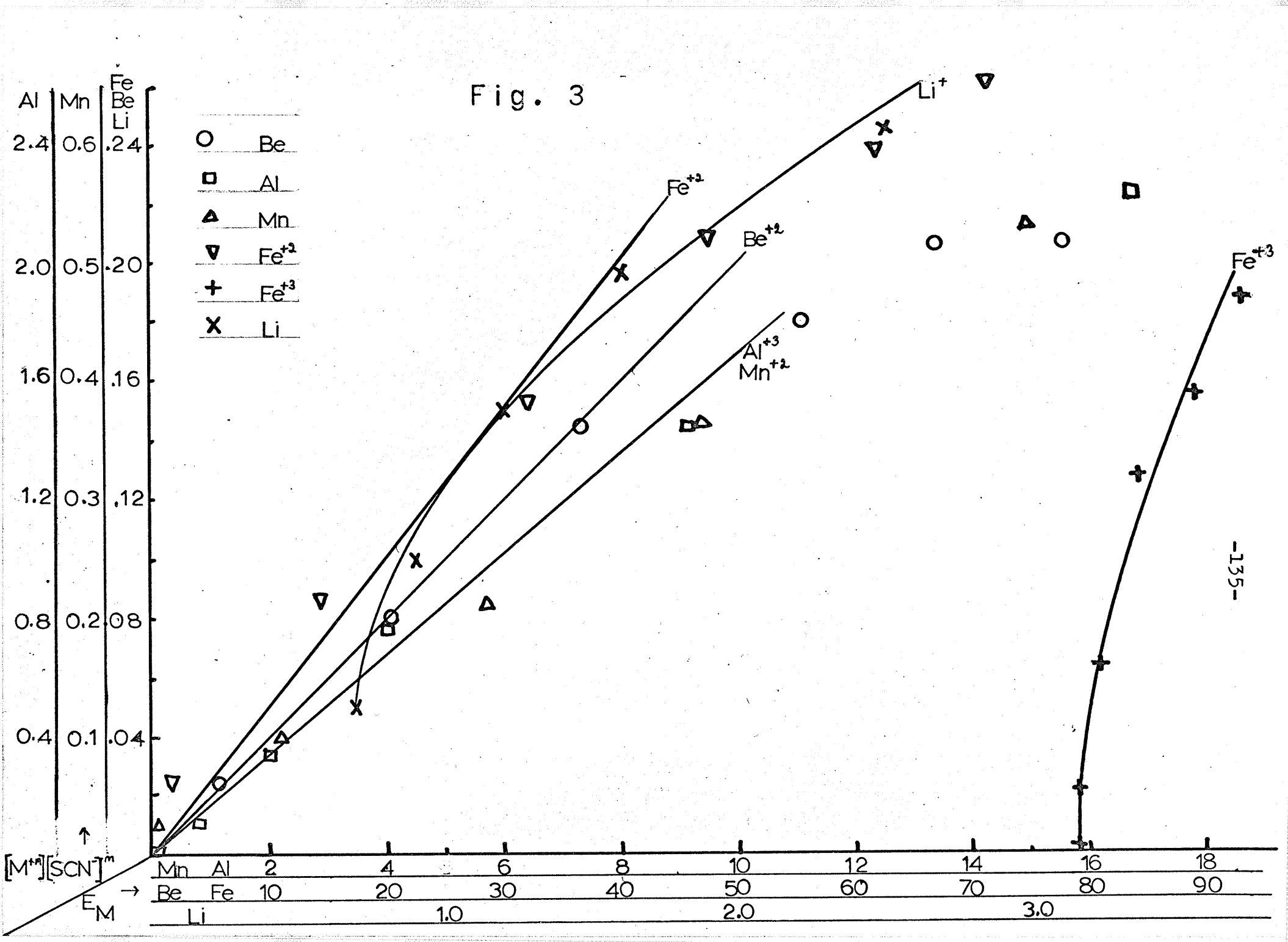

Al
Mn
Fe
Be
Li
2.4
0.6
.24
2.0
0.5
.20
1.6
0.4
.16
1.2
0.3
.12
0.8
0.2
.08
0.4
0.1
.04
Be
Al
Mn
Fe+2
Fe+3
Li
Li+
Fe+2
Be+2
Al+3
Mn+2
Fe+3
[M+n][SCN-]m
EM
Mn Al 2 4 6 8 10 12 14 16 18
Be Fe 10 20 30 40 50 60 70 80 90
Li 1.0 2.0 3.0

TABLE XXI

Effect of pH of aqueous solution on E_{Be} in terms of relation $E_{Be} = k\frac{(Be^{+2})_{aq.eq.}}{(SCN^-)^2_{aq.eq.}}$

	Methyl isobutyl ketone						1-Hexanol					
PpH	(SCN^-)	$(SCN^-)^2_x$	(Be^{+2}) total	(Be^{+2}) free* y	xy	E_{Be}	(SCN^-)	$(SCN^-)^2_x$	(Be^{+2}) total	(Be^{+2}) free* y	xy	E_{Be}
0.3	1.00	1.00	0.100	0.100	0.100	0.00	0.98	0.96	0.092	0.092	0.088	8.0
0.6	1.20	1.44	0.081	0.081	0.117	19.0	1.36	1.85	0.075	0.075	0.139	25.0
0.8	1.54	2.37	0.072	0.172	0.171	28.0	1.58	2.50	0.068	0.068	0.170	32.0
1.0	1.73	3.00	0.066	0.066	0.199	34.0	1.75	3.07	0.061	0.061	0.187	39.0
1.5	1.81	3.28	0.057	0.057	0.187	43.0	1.84	3.39	0.050	0.050	0.169	50.0
2.9	1.85	3.42	0.054	0.053	0.182	46.0	1.87	3.50	0.045	0.044	0.154	55.0
2.5	1.86	3.46	0.054	0.051	0.176	46.0	1.88	3.54	0.044	0.041	0.145	56.0
3.0	1.86	3.46	0.058	0.047	0.165	42.0	1.86	3.46	0.047	0.039	0.135	53.0
3.5	1.93	3.72	0.064	0.037	0.138	36.0	1.91	3.65	0.053	0.033	0.120	47.0
4.0	1.95	3.80	0.074	0.026	0.099	26.0	1.90	3.62	0.062	0.021	0.076	38.0
4.5	1.97	3.88	0.085	0.014	0.055	15.0	1.95	3.80	0.075	0.019	0.072	25.0
5.0	2.00	4.00	0.099	0.005	0.020	1.0	1.98	3.92	0.091	0.005	0.019	9.0

* $(Be^{+2})_{free}$ calculated from $K_{f_{BeOH^+}} = 1.90 \times 10^{10}$ [85]

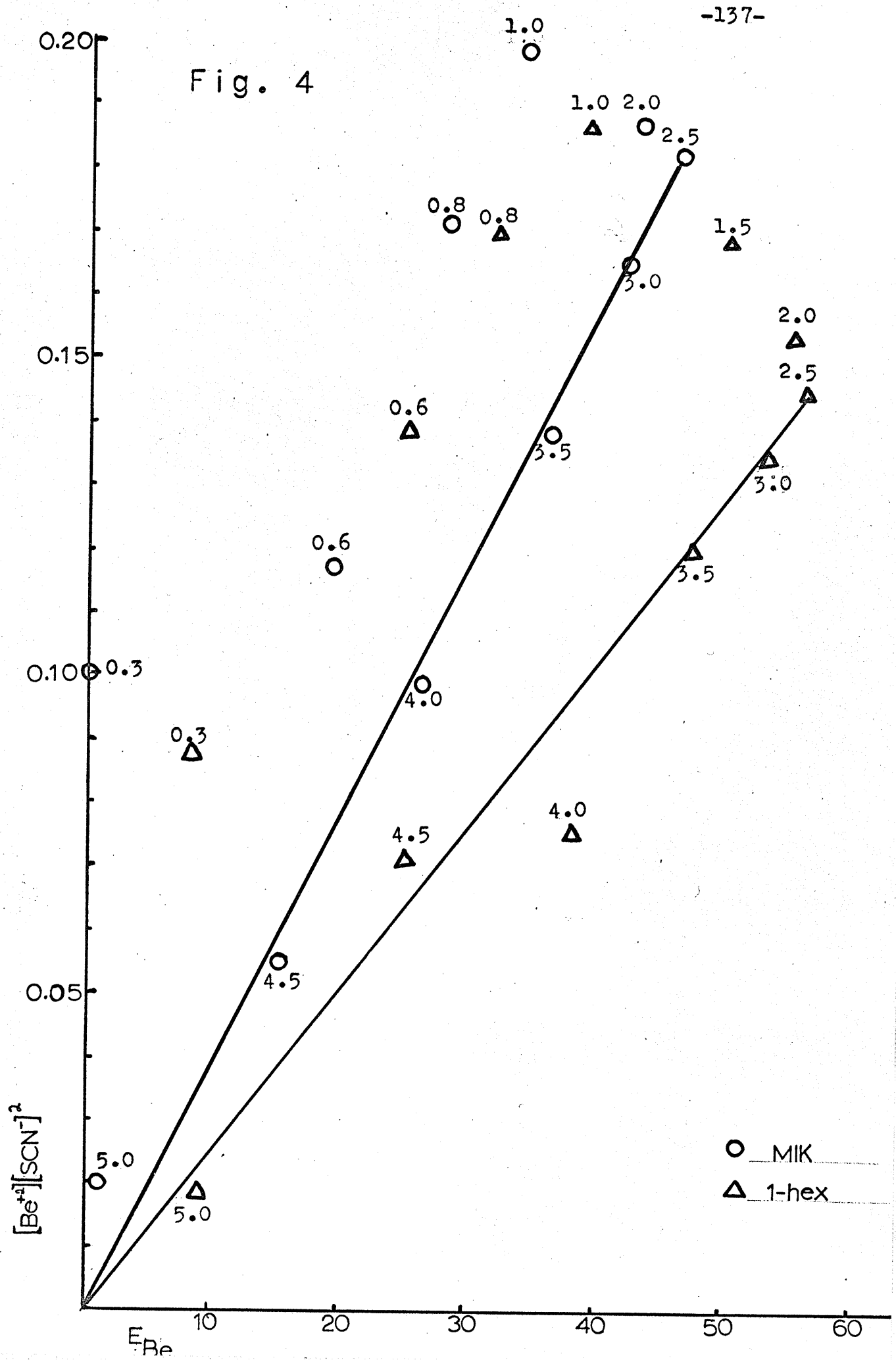
Fig. 4

The Effect of the pH of the Aqueous Phase on the Extraction of Beryllium Thiocyanate into 1-Hexanol and into Methyl Isobutyl Ketone in Terms of the Relation $E_{Be} = k(\left(Be^{+2}\right)_{\substack{equil. \\ aq.}})(\left(SCN^{-}\right)_{\substack{equil. \\ aq.}})^2$

The concentrations of the beryllium ion in the aqueous solutions at equilibrium are obtained from the pH's and the formation constant of the $BeOH^+$ ion, the concentration of the thiocyanate ion in the same solutions are calculated from the initial concentration and the distribution coefficient of thiocyanate into solvent at given pH's (see page 116). The products $\left(Be^{+2}\right)\left(SCN\right)^2$ for the solutions at equilibrium are then plotted against E_{Be}. See table XXI.

Numbers by the points indicate the pH of the aqueous solutions to which the points refer.

Fig. 4


0.20
0.15
0.10
0.05
$[Be^{+2}][SCN^-]^2$
10
20
30
40
50
60
E_{Be}
MIK
1-hex
1.0
1.0
2.0
2.5
0.8
0.8
1.5
3.0
2.0
2.5
0.6
3.5
3.0
0.6
3.5
0.3
0.3
4.0
4.0
4.5
4.5
4.0
5.0
5.0

FIGURES 5 to 10, EXPLANATORY NOTES

These figures show the absorption spectra in the near infra red of water in organic media of the following natures:

(a) A pure organic solvent.

(b) The same solvent equilibrated with an aqueous beryllium-thiocyanate-solution. The reference solution here is the same solvent equilibrated with an aqueous solution of the same thiocyanate concentration and pH as the aqueous beryllium-thiocyanate solution but lacking the beryllium, i.e., the reference solution is a "blank extract".

(c) The same solvent equilibrated with an aqueous beryllium-thiocyanate solution, the reference solution here being the pure solvent.

(d) The same solvent equilibrated with an aqueous aluminum-thiocyanate solution, the reference solution being a "blank extract" as in (b).

(e) The same solvent equilibrated with an aqueous aluminum-thiocyanate solution, the reference solution being the pure solvent.

The letters (a), (b), etc. are used to identify the spectra with the above notes. Not all of these spectra are contained in each set. The "(a)" spectra show the

effect that the nature of the solvent medium has on the absorption spectrum of the water, the "(b)" and "(d)" spectra show the absorption peaks of the water associated with the beryllium or aluminum-thiocyanate extracted species, and the "(c)" and "(e)" spectra show the absorption peaks due to the extracted metal thiocyanate species plus those due to water which is bound only to the solvent or to the thiocyanate and solvent.

The relative heights of the absorption peaks on these spectra are shown only approximately to scale, but the wavelength scales of the spectra on a given page are aligned above each other. Wavelengths are indicated in millimicrons (mμ). The vertical scale reads in optical density (O.D.).

Tables XXII - XXVIII give quantitative data on these absorption spectra.

Fig. 5 (a)

The Near Infra Red Absorption Spectrum of Water in Chloroform Solution.

5a

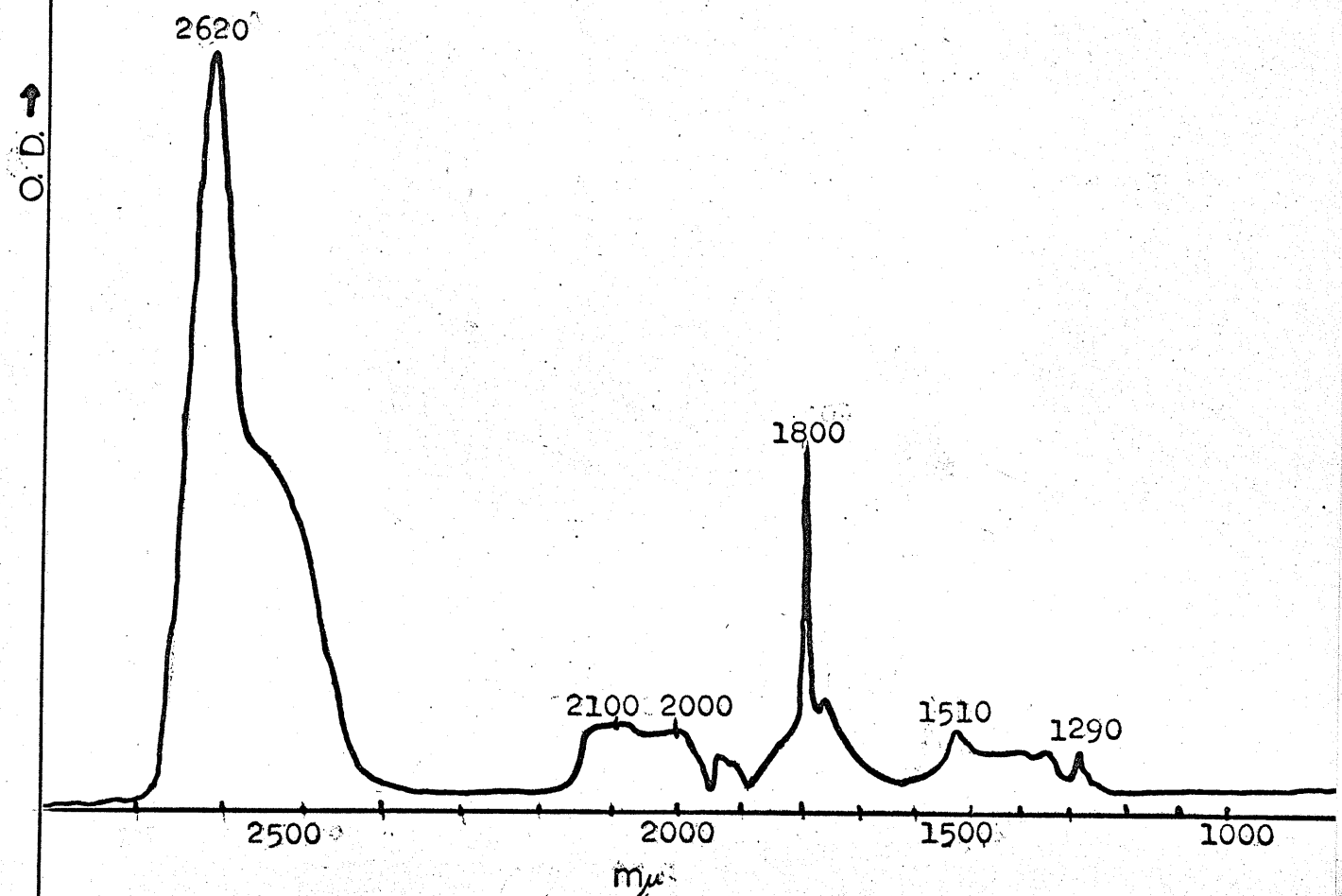


Fig. 6

(a) Water in MIK vs. MIK

(b) Beryllium Thiocyanate Extract in MIK
vs. "Blank Extract"

(c) Beryllium Thiocyanate Extract in MIK vs. MIK

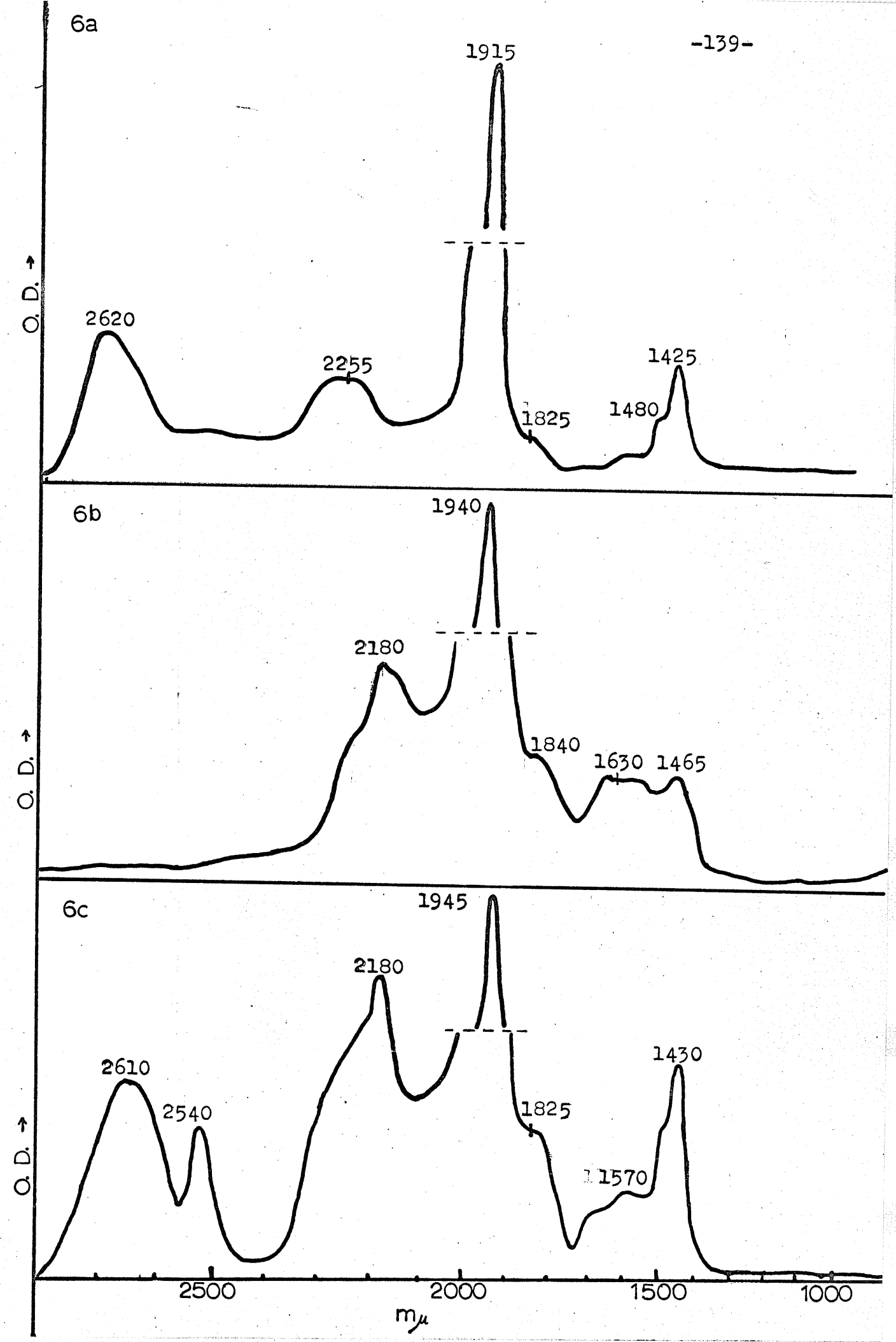

6a
1915
2620
2255
1825
1480
1425
O. D.
6b
1940
2180
1840
1630
1465
O. D.
6c
1945
2180
2610
2540
1825
1570
1430
O. D.
2500
2000
1500
1000
mμ

Fig. 6 continued

(d) Aluminum Thiocyanate Extract in MIK vs. #Blank Extract"

(e) Aluminum Thiocyanate Extract in MIK vs. MIK

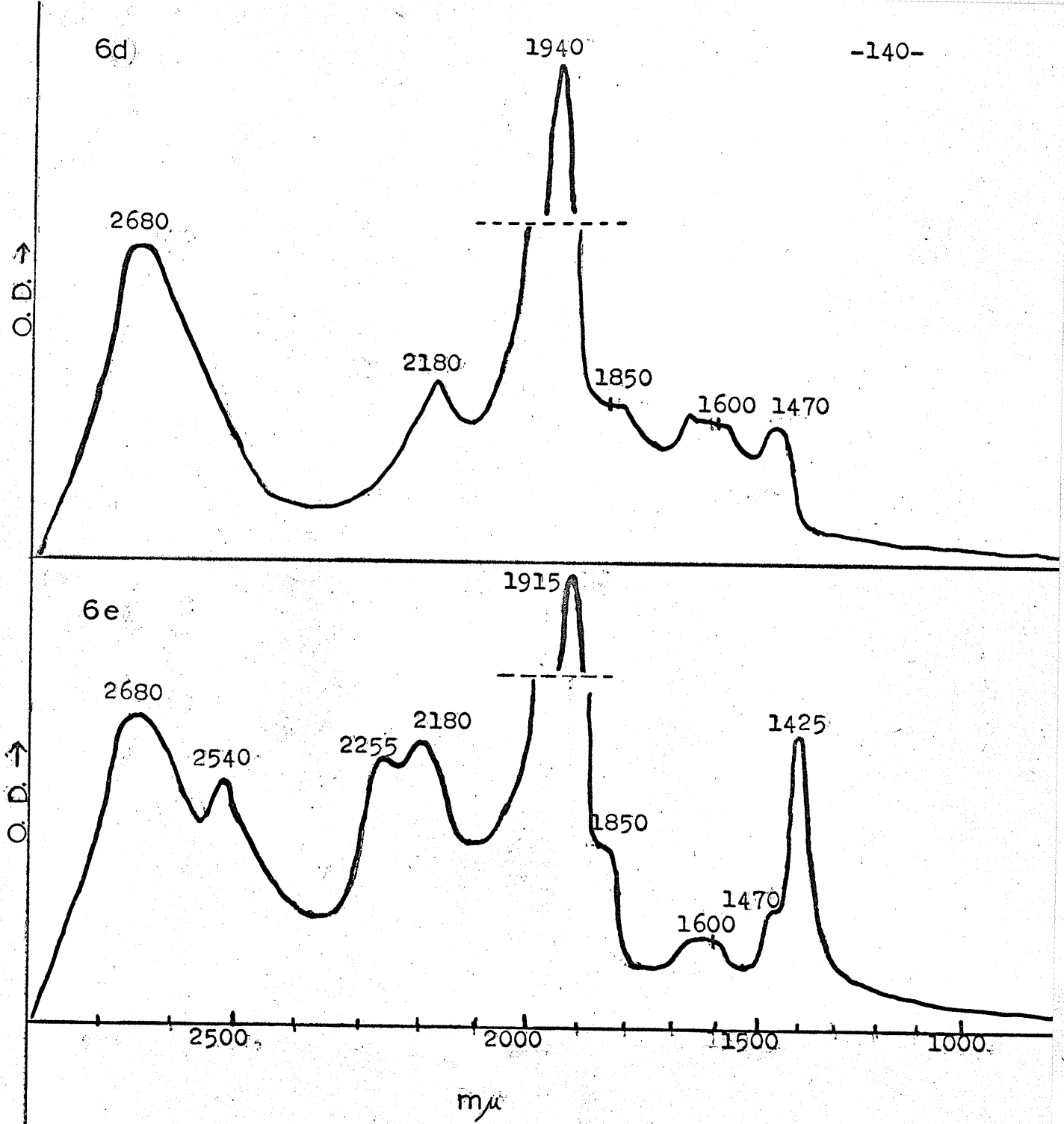

6d
1940
2680
2180
1850
1600
1470
O.D.
6e
1915
2680
2540
2255
2180
1425
1850
1470
1600
O.D.
2500
2000
1500
1000
mμ

Fig. 7

(a) Water in Butyraldehyde in Butyraldehyde

(b) Beryllium Thiocyanate Extract in Butyraldehyde vs. "Blank Extract"

(c) Beryllium Thiocyanate Extract in Butyraldehyde vs. Butyraldehyde

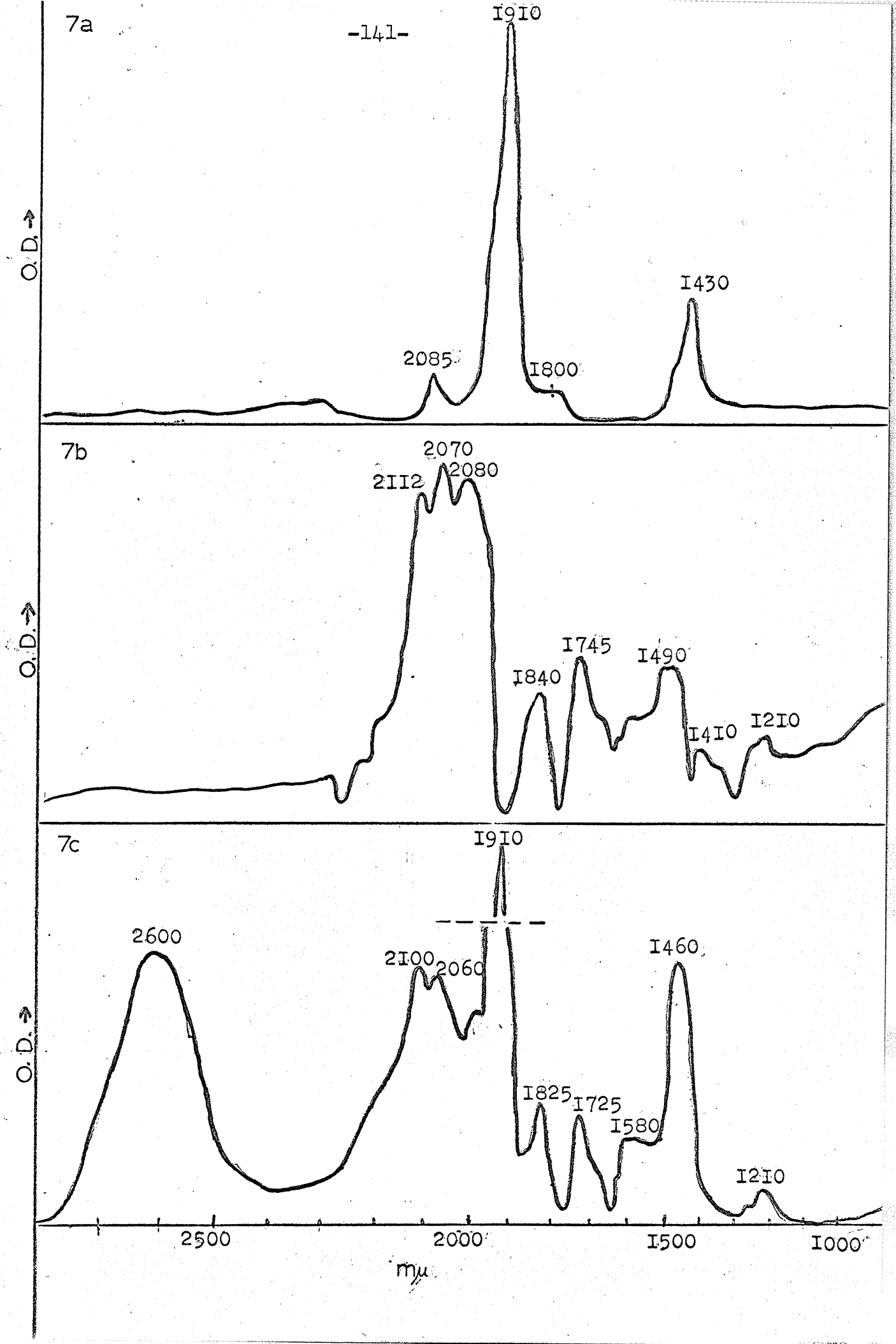

7a
1910
2085
1800
1430
O.D.
7b
2070
2080
2112
1840
1745
1490
1410
1210
O.D.
7c
1910
2600
2100
2060
1460
1825
1725
1580
1210
O.D.
2500
2000
1500
1000
mμ

Fig. 8

(a) Water in 1-Hexanol vs. 1-Hexanol

(b) Beryllium Thiocyanate Extract in 1-Hexanol vs. "Blank Extract"

(c) Beryllium Thiocyanate Extract in 1-Hexanol vs. 1-Hexanol

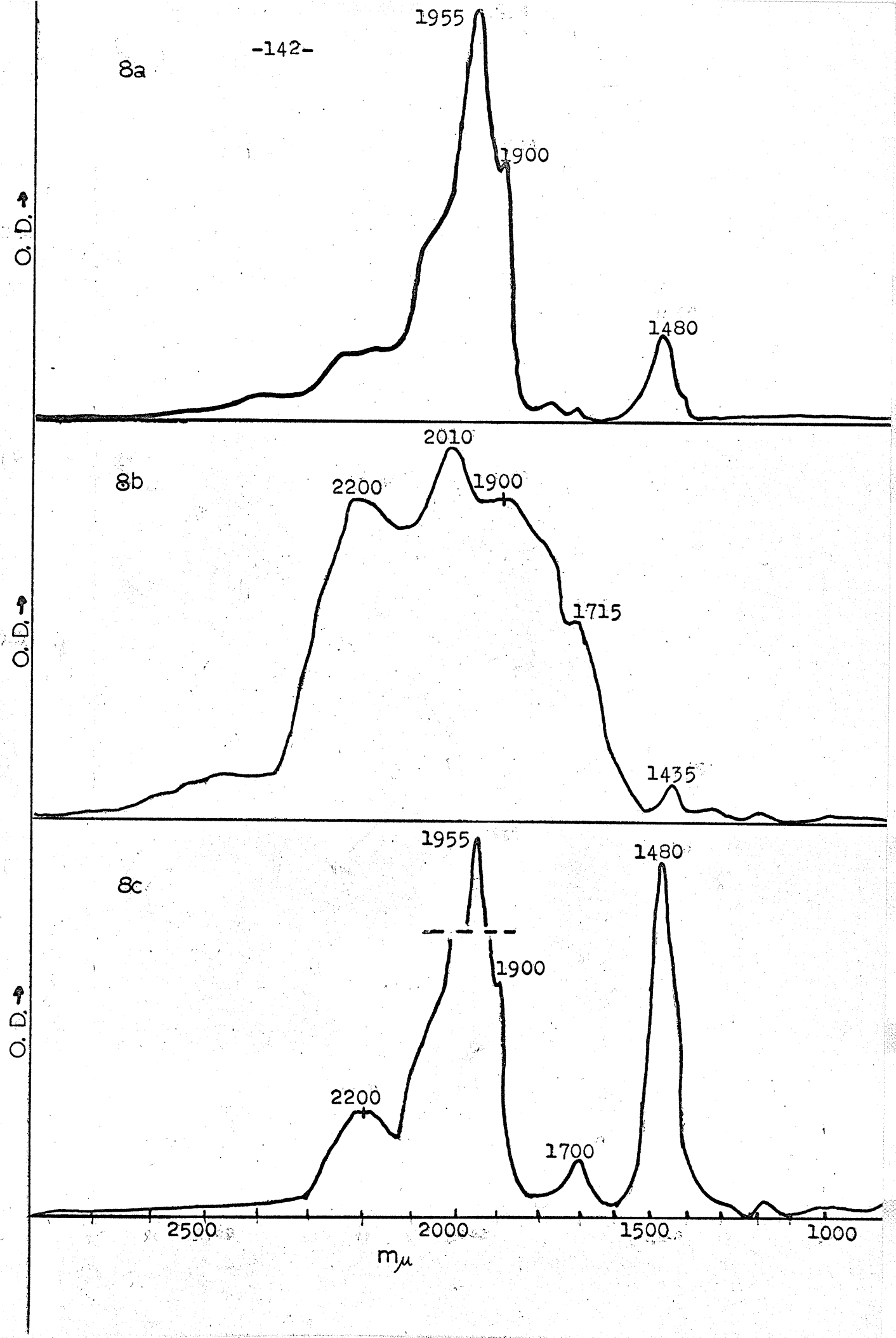

8a
1955
1900
1480
O. D.
8b
2010
2200
1900
1715
1435
O. D.
8c
1955
1480
1900
2200
1700
O. D.
2500
2000
1500
1000
mμ

Fig. 9

(a) Water in Ethyl Acetate vs. Ethyl Acetate

(b) Beryllium Thiocyanate Extract in Ethyl Acetate vs. "Blank Extract"

(c) Beryllium Thiocyanate Extract in Ethyl Acetate vs. Ethyl Acetate

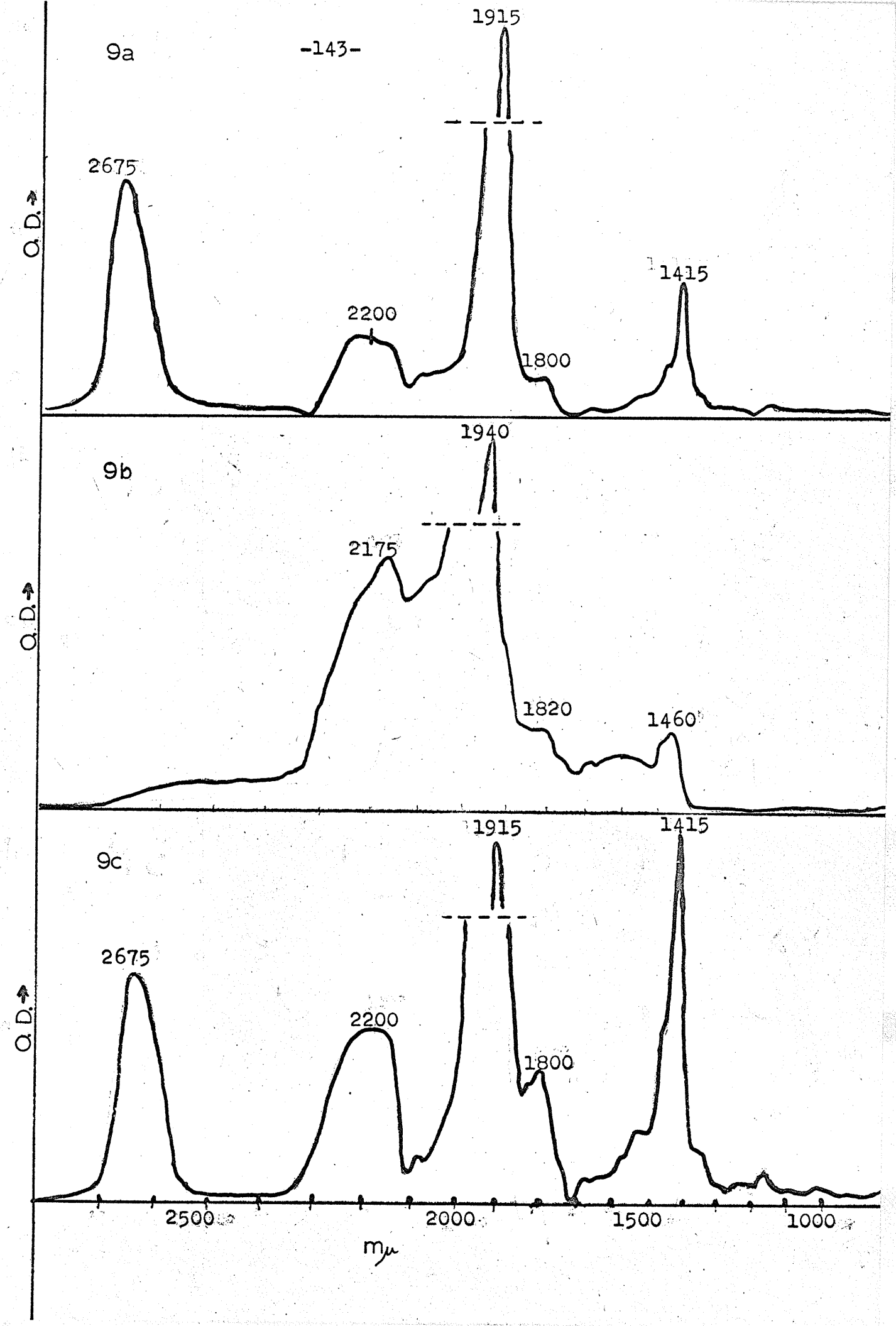

9a
1915
2675
2200
1800
1415
O.D.
9b
1940
2175
1820
1460
O.D.
9c
1915
1415
2675
2200
1800
O.D.
2500
2000
1500
1000
mμ

Fig. 10

(a) Water in Ethyl Ether vs. Ethyl Ether

(b) Beryllium Thiocyanate Extract in Ethyl Ether vs. "Blank Extract"

(c) Beryllium Thiocyanate Extract in Ethyl Ether vs. Ethyl Ether

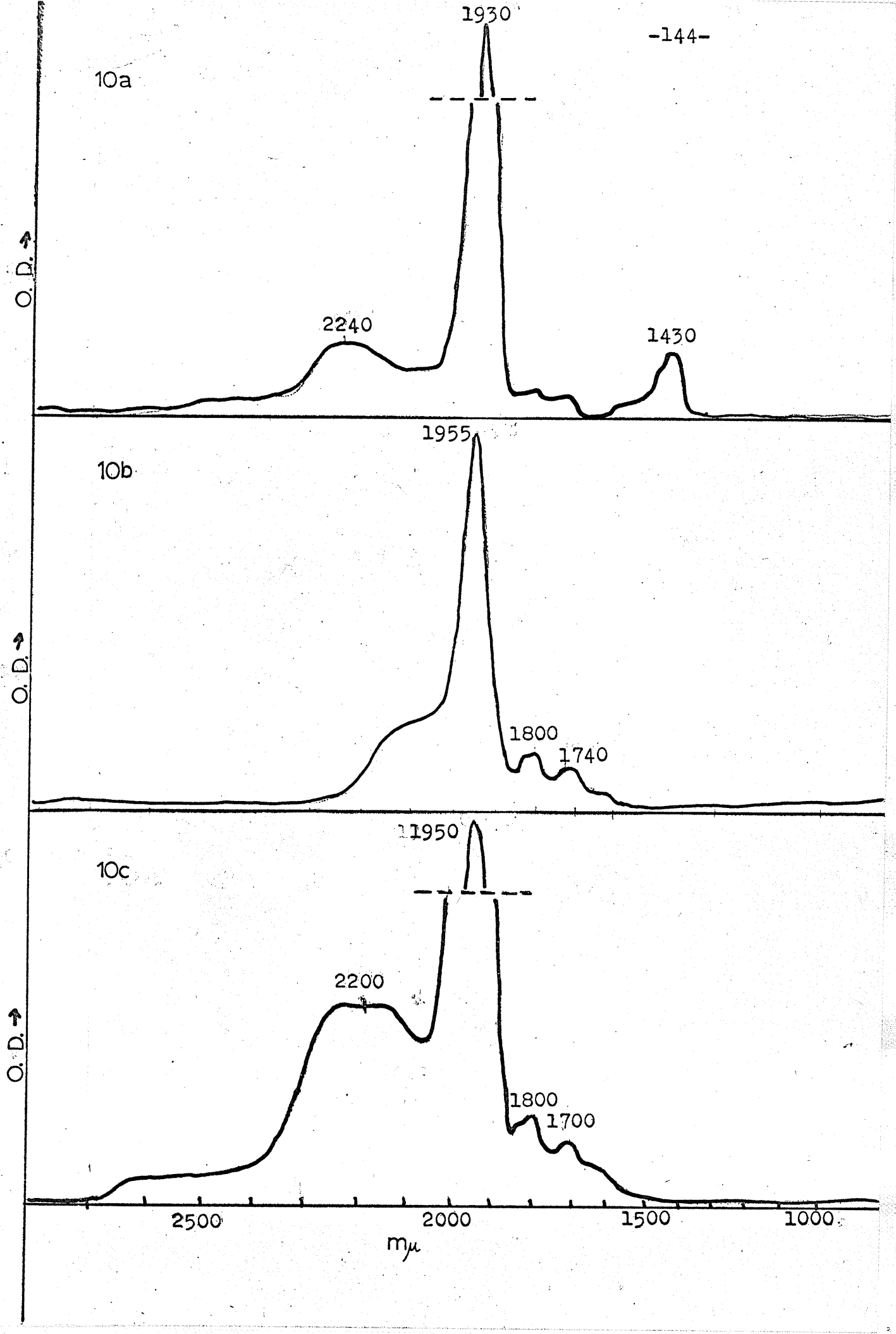

10a
1930
2240
1430
O.D.
10b
1955
1800
1740
O.D.
10c
1950
2200
1800
1700
O.D.
2500
2000
1500
1000
mμ

TABLE XXII

Relation of height of absorption peaks of H_2O in MIK to H_2O concentration

(H_2O) in MIK	Height (optical density at maximum) of peak at:					
	1425 mμ	1480 mμ	1820 mμ	1915 mμ	2250 mμ	2620 mμ
.055	0.021	0.018	0.019	0.079	0.030	0.022
.111	0.031	0.022	0.021	0.162	0.033	0.041
.222	0.046	0.025	0.027	0.407	0.050	0.053
.332	0.064	0.026	0.031	0.896	0.058	0.062
.443	0.077	0.030	0.035	-	0.066	0.066
.554	0.094	0.031	0.041	-	0.086	0.063
.665	0.114	0.039	0.048	-	0.096	0.071
.776	0.132	0.042	0.053	-	0.109	0.073

TABLE XXIII

Relation of peak height in absorption spectra of beryllium extracts in MIK to the beryllium content of the extract. Initial aqueous solution: (NH_4SCN) = 3.00, pH = 3.00, $(BeSO_4)$ as shown

No.	(Be^{+2}) in. aq.	(Be^{+2}) MIK	Peak Ht. (O.D max.) vs. blank ext. 1465 mμ	1630 mμ	1840 mμ	1940 mμ	2180 mμ	Peaks vs. MIK 2540 mμ	2690 mμ
1	0.0125	0.0094	0.000	0.000	0.000	0.027	0.013	0.088	0.157
2	0.025	0.0188	0.004	0.005	0.006	0.085	0.032	0.071	0.124
3	0.050	0.0360	0.019	0.016	0.018	0.188	0.069	0.072	0.124
4	0.075	0.0540	0.031	0.028	0.028	0.330	0.116	0.095	0.142
5	0.100	0.0710	0.035	0.031	0.031	0.492	0.142	0.096	0.147
6	0.150	0.104	0.050	0.045	0.046	1.553	0.215	0.101	0.145
7	0.200	0.135	0.069	0.061	0.068	-	0.295	0.131	0.180
8	0.300	0.194	0.086	0.078	0.089	-	0.428	0.116	0.158
9	0.400	0.248	0.099	0.088	0.100	-	0.558	0.158	0.212
10	0.500	0.295	0.114	0.101	0.123	-	0.745	0.128	0.171
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.064	0.124

TABLE XXIV

Relation of peak height in absorption spectra of aluminum extracts in MIK to aluminum content of the extract. Aqueous solutions: initially (NH_4SCN) = 3.00M, $(AL(NO_3)_3)$ as shown, pH = 3.00

No.	Initial aqueous (Al^{+3})	(NH_4SCN)	(Al^{+3}) MIK *	Peak (O.D)max. vs. blank extract 1470mμ	1600mμ	1850mμ	1940mμ	2180mμ	2680mμ	Peak vs. MIK 2540mμ
11	0.050	3.00	0.0065	0.008	0.008	0.012	0.048	0.026	0.00,	0.100
12	0.075	3.00	0.0096	0.011	0.012	0.012	0.078	0.035	0.015	0.128
13	0.100	3.00	0.0127	0.014	0.014	0.021	0.112	0.051	0.013	0.131
14	0.150	3.00	0.0188	0.022	0.017	0.026	0.190	0.069	0.030	0.137
15	0.200	3.00	0.0246	0.023	0.023	0.033	0.249	0.089	0.048	0.158
16	0.300	3.00	0.036	0.034	0.034	0.049	0.516	0.142	0.071	0.192
17	0.400	3.00	0.046	0.046	0.045	0.064	1.42	0.201	0.114	0.243
18	0.488	2.93	0.049	0.040	0.040	0.052	0.68	0.153	0.125	0.236
19	0.577	2.88	0.056	0.047	0.048	0.061	1.13	0.180	0.165	0.271
20	0.735	2.74	0.057	0.047	0.053	0.069	1.19	0.193	0.168	0.284
21	0.892	2.68	0.061	0.055	0.058	0.084	-	0.248	0.211	0.312
0	0.00	3.00	0.000	0.00	0.00	0.000	0.00	0.00	0.00	0.090

* The concentrations in columns 2 and 3 were obtained from the initial concentrations of the solutions and their volume changes on adjustment of pH to 3.00. The EAl expected at the concentration of Al^{+3} in the aqueous was then read from a plot of EAl against $(Al^{+3})_{aq.}$ and corrected for the changed (NH_4SCN) by the relation

$$(EAl)_2 = (EAl)_1 \left(\frac{(SCN^-)_2}{(SCN)_1} \right)^3$$

TABLE XXV

Relation of peak height to beryllium content of extract

Solvent: Butylraldehyde , aqueous phase (initial)

$[NH_4SCN]$ = 3M, pH = 3, $[BeSO_4]$ as shown

$[Be^{+2}]$ initial aqueous	$[Be^{+2}]$ ext.	Optical Density at 1210 mμ	1410 mμ	1500 mμ	1745 mμ	1840 mμ	2010 mμ	2070 mμ	2112 mμ
0.10	0.071	.009	.003	.021	.033	.017	.053	.075	.064
0.20	0.142	.016	.007	.038	.058	.033	.100	.128	.112
0.40	0.284	.042	.036	.068	.074	.058	.155	.161	.147

TABLE XXVI

Relation of peak heigh to beryllium content of extract

Solvent: 1-hexanol, aqueous solution (initial)

$[NH_4SCN]$ = 3M, pH = 3, $[BeSO_4]$ as shown

$[Be^{+2}]$ initial aqueous	$[Be^{+2}]$ extract	Optical density at 1435 mμ	1715 mμ	1900 mμ	2019 mμ	2200 mμ
0.10	0.072	0.00	.028	.046	.059	.050
0.20	0.144	.009	.045	.071	.092	.074
0.40	0.288	.014	.077	.135	.159	.133

TABLE XXVII

Relation of peak height to beryllium content of extract

Solvent: ethyl acetate, aqueous solution (initial): $[NH_4SCN]$ = 3M, pH = 3, $[BeSO_4]$ as shown

$[Be^{+2}]$ initial aqueous	$[Be^{+2}]$ extract	Optical Density at 1460 mμ	1820 mμ	1940 mμ	2175 mμ
0.10	0.059	.014	.013	.244	.066
0.20	0.118	.034	.030	.393	.101
0.40	0.236	.082	.076	--	.282

TABLE XXVIII

Relation of peak height to beryllium content of extract.

Solvent: ethyl ether, aqueous solution (initial):

$[NH_4SCN]$ = 3M, pH = 3, $[BeSO_4]$ as shown

$[Be^{+2}]$ initial aqueous	$[Be^{+2}]$ extract	Optical Density at 1490 mμ	1720 mμ	1800 mμ	1955 mμ
0.10	0.012	0.00	0.00	0.00	.050
0.20	0.024	0.00	.010	.012	.102
0.40	0.048	.008	.027	.033	.277

TABLE XXIX

Relation of total water content of M1K extracts of beryllium thiocyanate to beryllium content

Initial aqueous solution: $[NH_4SCN]$ = 3.00M

$[BeSO_4]$: as shown

pH = 3.00

Solvent: M1K

Water concentration determined by Karl Fisher titration

Number of extracts correspond to those in Table XXIII

No.	$[BeSO_4]$ (initial aqueous)	$[Be^{+2}]$ (M1K)	$[H_2O]$ (M1K)	Notes
H_2O	0.0	0.0	0.864	M1K, H_2O-saturated
-	0.0	0.0	0.001	initial M1K
0	0.0	0.0	0.746	"blank extract"
1	0.0125	0.0094	0.802	
2	0.0250	0.0188	0.871	
3	0.050	0.036	0.978	
4	0.075	0.054	1.07	
5	0.100	0.071	1.13	
6	0.150	0.104	1.32	
7	0.200	0.135	1.48	
8	0.300	0.194	1.69	
9	0.400	0.248	1.82	
10	0.500	0.295	1.90	

Fig. 11

Plot of the Total Water Concentration of MIK Extracts of Beryllium Thiocyanate Against the Beryllium Concentration of the Same Extracts

The slope (m) of the line through any point on the curve represents the hydration of the extracted species at that concentration. See table XXIX.

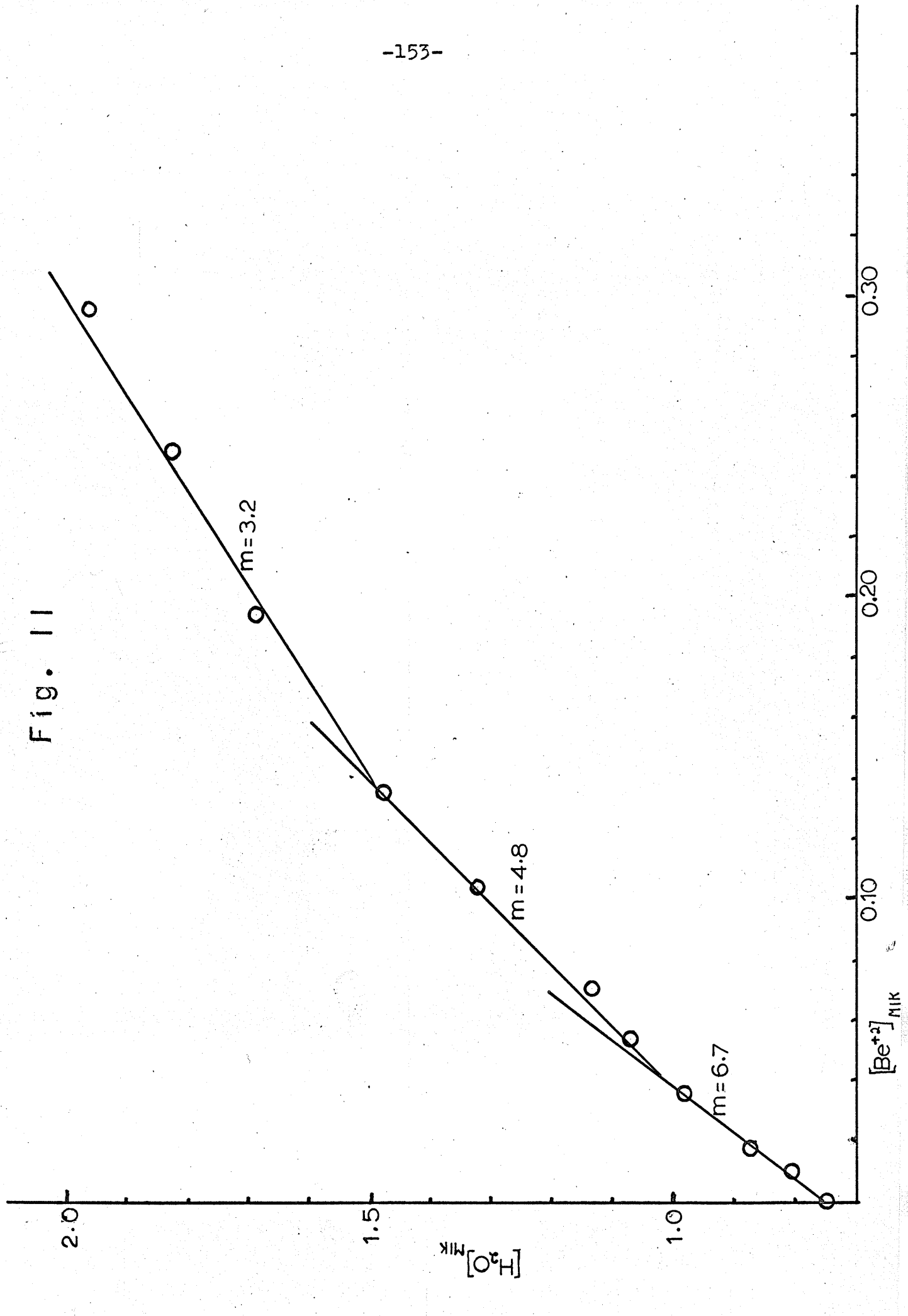


Fig. 11

TABLE XXX

Relation of total water content of MIK extracts of aluminum thiocyanate to aluminum content

Initial aqueous solution $[NH_4SCN]$ = 3.00 M

$[Al(NO_3)_3]$ = as shown

pH = 3.00

Solvent: MIK

Water concentration determined by Karl Fisher titration.

Numbers of extracts correspond to those in Table XXIV.

Concentrations of aluminum in extract phases determined as explained there.

No.	$[AlNO_3]$ (initial aqueous)	$[Al^{+3}]$ (MIK)	$[H_2O]$ (MIK)	Notes
0	0.00	0.00	0.753	"blank extract"
11	0.050	0.0065	0.819	
12	0.075	0.0096	0.847	
13	0.100	0.0127	0.868	
14	0.150	0.0188	0.893	
15	0.200	0.0246	0.959	
16	0.300	0.036	1.02	
17	0.400	0.046	1.18	
18	0.488	0.049	1.20	
19	0.577	0.056	1.27	
20	0.735	0.057	1.29	
21	0.892	0.061	1.32	

Fig. 12

Plot of the Total Water Concentration of MIK Extracts of Aluminum Thiocyanate Against Aluminum Concentration of the Same Extracts.

The slope (m) of the line through the points indicates the hydration of the extracted species. See table XXX.

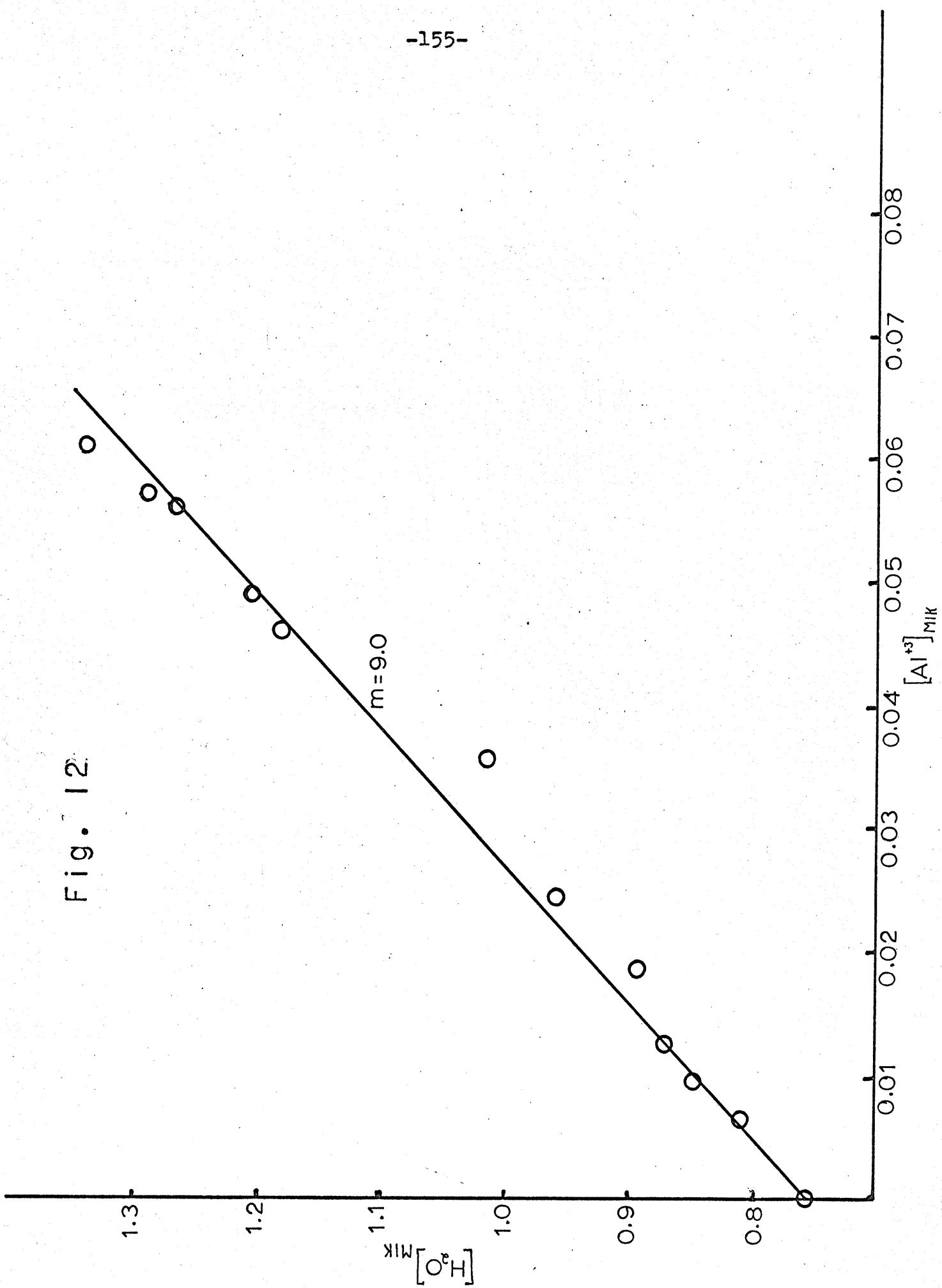
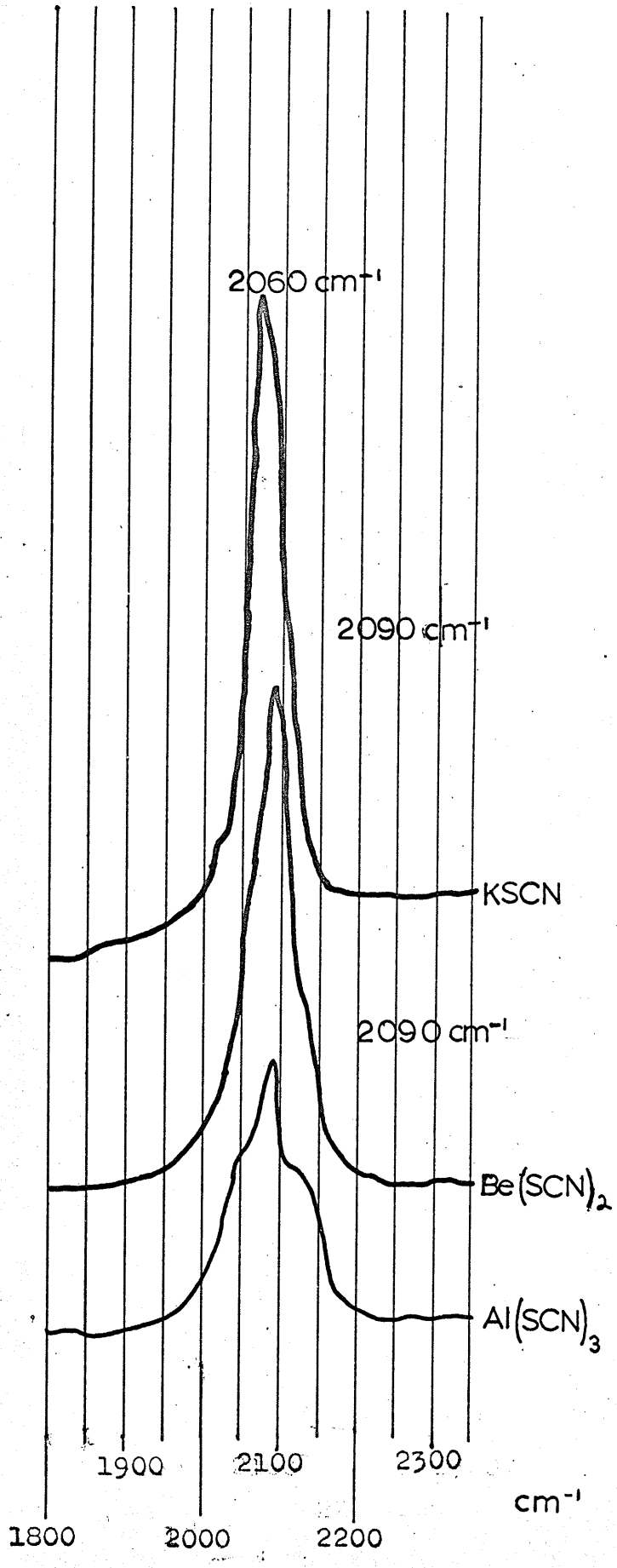

m=9.0
$[H_2O]_{MIK}$
$[Al^{+3}]_{MIK}$
0.8
0.9
1.0
1.1
1.2
1.3
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08

Fig. 12

Fig. 13

The absorption bands of the thiocyanate ions in solid beryllium-, aluminum-, and potassium thiocyanates in the infra red region are shown here, identified by the formulae of their salts.

Fig. 13


2060 cm⁻¹
2090 cm⁻¹
KSCN
2090 cm⁻¹
Be(SCN)2
Al(SCN)3
1900
2100
2300
cm⁻¹
1800
2000
2200

Section 5: DISCUSSION

The data on the extraction of beryllium and aluminum ions with halide and pseudohalide ions might be taken to indicate that the predictions made on pages 99 - 102 are correct. Beryllium does indeed extract to a greater extent than aluminum with such ions, and the species formed by the anion and the beryllium or aluminum ion is not a complex anion but a neutral species. The greater extraction of the beryllium species is presumably due to its greater stability which results in its formation to a greater extent under any set of conditions. The greater stability of the beryllium species must in turn be due to the greater polarizing power of the beryllium II ion as compared with aluminum III. Of the factors governing the stability of a complex which a cation can form beryllium differs from aluminum only in its polarizing power.

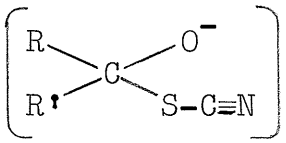
However the extracting beryllium or aluminum cation has been shown to be hydrated to an extent which precludes the possibility that a beryllium or aluminum thiocyanate complex is formed. This is a common feature of the extraction of coördinately solvated salts or complex metal acids[69,70,76]; the first coördination sphere of the cation is the same regardless of whether the cation is in the aqueous phase or the organic phase. Where, as here, the extracting species is a coördinately solvated salt, the

association between the anion and cation is one of ion pairing, but not one of complexation of the cation by the anion. The cation is complexed by the water molecules, or in some cases by the organic solvent molecules.

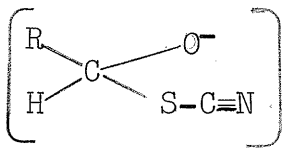
Since the hydrated beryllium ion is smaller than the hydrated aluminum ion the greater polarizing power of the former can still be invoked to explain the greater stability and extractability of the beryllium - halide or - pseudohalide species.

Since the description of chemical species in the thiocyanate system is somewhat involved it will be well to consider it under a number of headings, the first of which is:

Extracting Thiocyanate Species. The data (page 124) indicate that the extracted thiocyanate ion is strongly solvated, not only by alcohols, but also by ketones and aldehydes, this solvation going as far as the formation of unstable compounds. The solvates formed by thiocyanate with ketones and aldehydes are probably of the sort which are known to be formed by cyanide and these organic compounds:

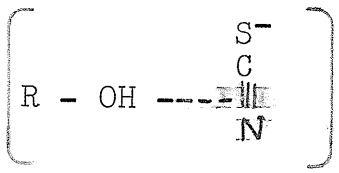


NH_4^+ or H_3O^+ with ketones and



NH_4^+ or H_3O^+ with aldehydes

To explain the solvation in alcohols, and a number of other phenomena, hydrogen bonding to the triple bond of the thiocyanate ion is postulated. This seems reasonable because a large concentration of electron density must exist between the carbon and nitrogen atoms (the triple bond has been shown to exist by Raman spectra[80]) and because many reactions of thiocyanate can only be explained by hydrogen bonding. On the basis of this hypothesis the alcohol solvate would have the structure:



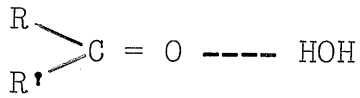
NH_4^+ or H_3O^+

It is probable that thiocyanate is also solvated by esters and ethers, but that the solvation here is weaker. The fact that solvation of the anion takes place to some extent in all the solvents used would acoount for the fact that the decrease in the distribution coefficients on going from alcohols to other solvents is not as great as the decrease in solubility of inorganic salts noted by Garwin and Hixson[55].

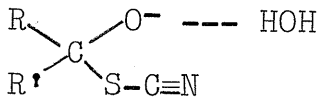
Hydrogen bonding to the triple bond of thiocyanate can also be used to explain two other puzzling features of thiocyanate extraction. The first of these is the bonding between water and thiocyanate in M1K solutions. This is revealed by the change in the absorption spectrum of water in M1K solution when thiocyanate

is added, resulting in changes in the molar absorpitivites of different absorption peaks, and the appearance of a new peak at 2540 mμ. The second is the fact that little ammonium thiocyanate is extracted from aqueous solution by MIK when the hydrogen ion concentration of the aqueous solution is in the region of 10^{-3} M, but at higher acidities where large amounts of thiocyanic acid are extracted ammonium thiocyanate also extracts readily. The presence of thiocyanic acid in the organic solvent enhances the extraction of ammonium thiocyanate. A possible explanation of these facts is as follows:

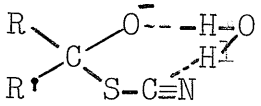
Water in the solvent MIK is hydrogen bonded to the ketone oxygen:



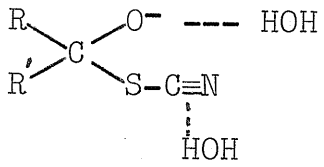
but in the presence of extracted thiocyanate it can also hydrogen-bond to the thiocyanate-ketone compound, Several different forms of the MIK-thiocyanate-water compound are possible and it is probable that all are present to some extent.



(1)



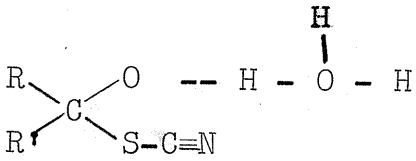
(2)



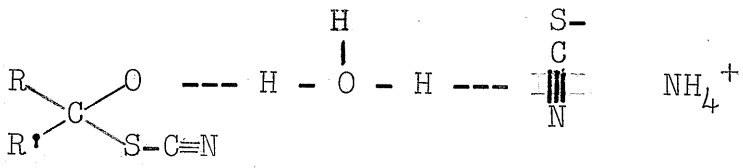
(3)

The formation of such groups would explain why water in thiocyanate - containing MIK solutions shows a different absorption spectrum from that of water in pure MIK solutions.

Extracted thiocyanic acid would have the form:



and further extracted ammonium thiocyanate could take the form



The three hydrogen atoms of the hydronium ion could all take part in hydrogen bonding in the same way that they do in bonding to solvent molecules[23, page 151]. The

presence of thiocyanic acid in the solvent could thus stabilize extracted ammonium thiocyanate. Ammonium thiocyanate is less extractable itself because its cation is less easily solvated. Thiocyanic acid is pictured here as extracting as H_3O^+ SCN^-. It may actually extract as $H_9O_4^+$ SCN^-, but this would not change these arguments.

Extracting Beryllium and Aluminum Species. The beryllium extracting species has been found to extract with from three to six water molecules. The amount of this water per beryllium ion depends on the concentration of the beryllium species in the organic (MIK) phase. Aluminum however always extracts with nine water molecules per aluminum ion. Since beryllium normally has a hydration number of four, and aluminum of six, some of this water must exist outside of the primary coördination sphere of the metal ions.

The role of the solvent toward the hydrated cations is clear. It has been shown that the solvent molecules interact with water dissolved in it and it evidentally interacts with the water molecules of the hydrated cations in the same way. The interaction is in both cases one of hydrogen bonding. Coördination of the water to the cation (Be^{+2} or Al^{+3}) would tend to draw negative charge away from the hydrogens of the water, leaving them more positive and capable of forming hydrogen bonds to the negative centre of the solvent molecule. Polar solvents with centre of negative charge near the surface of the molecules and with

large dielectric constants, which would be expected to solvate unhydrated cations best, are also the solvents which would form hydrogen bonds to water molecules most readily. This pictures an interaction of the hydrated cation with the solvent which is similar to that of the hydrated proton with solvents[23, page 151]. This seems reasonable since the hydrated aluminum or beryllium ion is not much larger than the hydrated proton, and carries a larger charge.

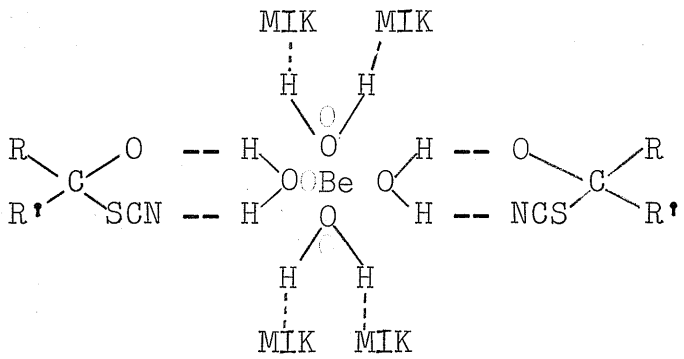
The extent of hydration of the extracting species has been found by plotting the total water content of the MIK extracts against the beryllium or aluminum concentration of the extracts, and taking the slope of the resulting line as equal to the hydration number. This method is open to some criticism in view of the results of Yates, Laran, Williams, and Moore[70]. The justifications for this procedure are as follows:

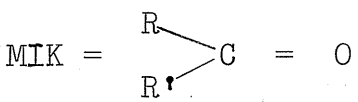
(1) In the case of aluminum extracts a straight line can be drawn through the points on the plot of $(H_2O)_{MIK}$ vs. $(Al^{+3})_{MIK}$ which passes through the point for $(H_2O)_{MIK}$ a t $(Al^{+3})_{MIK} = 0$.

(2) In the case of the beryllium extracts, the "free water" peaks in the absorption spectra show only erratic changes in height with increasing beryllium concentration. The fact that the "free water" peak in the spectra of the aluminum extracts increases with increasing aluminum concentration can be explained as below.

(3) The conclusions drawn from the data on hydration obtained in this way fits very well in the general picture of the extracting species to be drawn.

This general picture of the metal species in the MIK extracts can now be assembled. The beryllium ion extracts with four water molecules in its primary coördination sphere and a varying number of water molecules outside of this sphere. All these water molecules are hydrogen bonded to the oxygen atom of the ketone molecules. The solvent-thiocyanate species is also hydrogen bonded to the water of the primary solvation sphere of the beryllium ion. The beryllium-thiocyanate-water-solvent species must then have the structure:





The oxygens of the water molecules are of course tetrahedrally arranged about the beryllium ion, and there are other water-solvent pairs outside of the solvation sphere shown. The fact that all the water molecules of the beryllium species are not equivalent would account for the breadth of the absorption bands of water in the absorption spectra of these extracts.

Beryllium has a strong tendency to polymerize through water and this probably occurs in the extracts as the concentration of the beryllium species increases. This would lead to a less hydrated species and to the decrease in the hydration of the extracted species with increasing beryllium concentration in the extracts which is noted.

In the aluminum species the association between the hydrated aluminum ion and the solvent thiocyanate species is much weaker. For this reason the solvent-thiocyanate groups are bound to water molecules which are not part of the hydration sphere of the aluminum ion. Because of the larger size of the hydrated aluminum ion, it carries no water molecules outside of its primary hydration sphere. The aluminum extracted species has the form:

$$(Al(H_2O - MIK)_6^{+3})\ (MIK - SCN - H_2O)_3^-$$

The hydration number of the extracted species is thus nine. Since the aluminum ion has less tendency to polymerize through water molecules, and since the aluminum extracts never become as concentrated as those of beryllium do, there is no decrease in the hydration number of the extracted species with increasing concentration of the extracts.

The structure explains the fact that the absorption peak of the free water (water bound to the solvent-thiocyanate species) in the absorption spectra of aluminum extracts increases with the aluminum concentration; part of the "free water" is actually part of the extracted species. This is not the case in the beryllium extracts where the thiocyanate extracting with the metal ion is bound to the water of the hydration sphere of the beryllium ion, and hence carries no water "of its own".

Decrease of Extent of Extraction of Metals at Low pH. As has been stated earlier (page 115) part of the decrease in the extent of extraction of beryllium or aluminum from aqueous thiocyanate solutions at low aqueous pHs can be explained by the loss of thiocyanate to the organic phase. However the extent of the decrease of D_{Be} or D_{Al} at pH's below 2.5 is too great to be accounted for by this phenomenon alone.

Another phenomenon which could contribute its effect to decrease the extractions at low aqueous pH is the competition of the solvent-thiocyanic acid species for

for the thiocyanate ion in the organic phase. It has been shown above that the thiocyanic acid-solvent species can form hydrogen bonds to other extracted thiocyanate ions (page 161). This enhances the extraction of ammonium thiocyanate because the ammonium ion is held in the extract only by the electrostatic attraction of the thiocyanate anion. But it could lower the extraction of beryllium and aluminum because these metals must form ion pairs or hydrogen-bonded groups with the thiocyanate to be stable in the solvent. Thus thiocyanic acid in the solvent competes with the beryllium or aluminum species for the thiocyanate ion, and thereby lowers the extraction of these metals.

Polymerization of Beryllium or Aluminum Thiocyanate. In the aqueous phase beryllium thiocyanate does not form polynuclear or polymeric species except at very high concentrations. In the organic phase polymerization takes place through the water molecules of the hydration spheres of the cations, but not through the thiocyanate groups. That these statements are true is made clear by the fact that the distribution coefficient of beryllium thiocyanate is unaffected by the concentration of the beryllium.

Beryllium thiocyanate cannot polymerize in the aqueous phase because the beryllium ions are strongly hydrated. In the organic phase bridging by the thiocyanate groups

between the hydrated beryllium ions is prevented by the strong pairing of the hydrated beryllium ions and the thiocyanate groups through hydrogen bonding.

Aluminum would be expected to behave in the same way as beryllium in respect to polymerization, but the increase in distribution coefficients of aluminum thiocyanate at low concentrations can only be explained by some type of polymerization. The data of Table XV could be explained either by polymerization of the aluminum thiocyanate species in water at high concentrations (beginning at or below 10^{-4} M Al^{+3}) or in the organic solvent at low concentrations. The latter could take place as a result of polynucleation which only begins to take place when the thiocyanate to aluminum ratio in the extract exceeds a critical value. The amount of thiocyanate extracting into the MIK as ammonium thiocyanate is the same for all these extracts but the aluminum concentration in the MIK varies.

Polymerization of aluminum thiocyanate in the aqueous phase at concentrations as low as 10^{-4} M seems very unlikely, although polymerization of indium bromide at such concentrations in water has been postulated[71]. It is possible that it could take place here through hydrogen bonding of the thiocyanate to the water of the hydration sphere of the aluminum ions.

In solid beryllium or aluminum thiocyanate and in their concentrated aqueous solutions there can be no doubt of the occurrence of extensive polymerization. The infra red spectra of the thiocyanates (figure 13) do not clearly confirm or deny the existence of bridging thiocyanate groups in these compounds. The absorption band of thiocyanate occurs at a lower frequency in beryllium thiocyanate and aluminum thiocyanate than it does in potassium thiocyanate, but the absorption band for all these compounds falls at lower frequencies than that found by Chatt and Duncanson[73] for the thiocyanate group. Since the complexes here being dealt with are quite different from those of Chatt and Duncanson, exact correlation between their results and these could perhaps not be expected. Nonetheless the shift of the absorption band to lower frequencies is evidence for bridging thiocyanate in beryllium or aluminum thiocyanate.

Also the extreme viscosity of the concentrated solutions of beryllium or aluminum thiocyanate can hardly be interpreted as meaning anything but polymerization. An almost immobile syrup is obtained when solutions of these salts are concentrated in a flash evaporator even when no decomposition (which might produce the polymeric $BeOBe^{++}$ species) occurs, Crystallization from these syrups has so far not been obtained, although a glass of aluminum thiocyanate was once obtained.

Role of the Solvents in Extraction. The role of the solvents in further solvating the hydrated cations, and in solvating the thiocyanate anion has already been explained. In such a picture as this beryllium would be expected to extract to a greater extent than aluminum because, being a smaller ion with a smaller hydration sphere, the effective charge of its hydrated ion is greater than that of the hydrated aluminum ion, and hence its interaction with the solvent molecules through the water molecules of its hydration sphere is greater.

The order of the classes of organic solvents, arranged according to the extent to which they extract beryllium or aluminum from aqueous solutions of thiocyanate, was that predicted on page 103 . It is thus the order of the solvents according to their basicity and the steric availability of their donor atom. There is one striking exception however: organic acids which should be among the better extracting media[55] have no detectable extracting power. A possible explanation for this lies in the highly dimerized hydrogen-bonded structure of these solvents. This would render the donor oxygen atom of the acids unavailable for further bonding.

CHAPTER V

THE DEVELOPMENT OF A FLOW SCHEME FOR THE EXTRACTION OF BERYLLIUM FROM ORES

Section 1: INTRODUCTION

Large deposits of bertrandite ore are to be found in many parts of North America, and it is listed as one of the more important potential sources of beryllium by the National Security Resources Board of the U.S. Government[2]. This mineral has the composition indicated by the formula $Be_4(OH)_2(SiO_4|SiO_3)$ and as such has the theoretical beryllium oxide content of 42 percent. Actual deposits of the ore however usually contain only 0.5 - 1.0 percent beryllium oxide. As such it is a low grade ore (Beryl whose large crystals can be "cobbed" by hand usually contains about 10 percent beryllium oxide) and not suited to the type of extractive metallurgical processes used for beryl. No beneficiation process has been found to work on it. For these reasons, and because beryl deposits have been able to meet the current demands for beryllium, bertrandite deposits have gone untouched except for exploration and claiming.

This is in spite of the fact that bertrandite has certain advantages over beryl as a source of beryllium. It is found in much larger deposits and the overall bertrandite deposits are richer in beryllium than the overall beryl

deposits. The pegmatites in which beryl is found usually contain two or three percent of beryl. Most important, bertrandite is attacked by sulphuric acid at moderate temperatures, sometimes giving up its entire beryllium content to solution after a treatment with sulphuric acid. Presently used methods for the treatment of beryl call for elaborate heat treatment to "open" the ore and render its beryllium content acid leachable.

It was desired in this work to develop a flow scheme for the removal of beryllium oxide from a bertrandite ore by solvent extraction. It was hoped that this would be an economic process capable of continuous operation, and that it would produce beryllium oxide in a greater state of purity than does the present practice.

The sulphuric acid leaching of bertrandite ores had first to be investigated. For those ores which are completely acid leachable the most economic process of obtaining complete solution of the beryllium had to be found. Complications, such as the possibility that fluoride from the ore might complex the beryllium and render it inextractable had to be watched for. The best method of handling those bertrandite ores which are only partly leachable by sulphuric acid has yet to be determined. Since there are large deposits of completely acid leachable bertrandite work concentrated on these.

The treatment of the solution obtained from leaching also posed problems. These included the neutralizing

of the excess acid, reducing the aluminum content, and removing the iron. The last two metals are at least partly leached from the ore with the beryllium. Data were obtained which it is hoped will help clarify these, although the final answers will depend on economic as well as chemical factors.

Some time was spent in attempts to carry out countercurrent extraction of beryllium thiocyanate solutions in rotary or packed columns, or in a mixer-settler. The mixer-settler was built according to the plans of Alter, Codding, and Jennings[66, & 12, page 296] with some modifications. The columns regardless of height (to 8 feet), packing, flow rates, or volume ratios, never showed more than three theoretical stages. The mixer-settler likewise did not give efficient extraction. It is thought that this inefficient extraction results from the fact that, in these devices, the MIK is never divided into the colloidal dispersion observed in separatory funnel extractions with this solvent. Rapid attainment of equilibrium in this system apparently depends on this fine division of the solvent. Columns, of course, have been noted to be inefficient devices for solvent extraction elsewhere[12].

Because of these difficulties separatory funnels were used in obtaining data on countercurrent extraction of these beryllium solutions. The data presented here are not extensive but they demonstrate the potential of the method.

Data on stripping the extract and on thiocyanate recovery have previously been obtained (Chapter III). These, together with the data on ore leaching and countercurrent extraction are combined in the flow scheme presented at the end of section 4.

Section 2: PREVIOUS RELEVANT INVESTIGATIONS

Solvent extraction has been investigated as a step in the production of beryllium, but no attempt has previously been made to develop an entire flow scheme based on the use of this method of separation. Solvent extraction has been tested on a pilot plant scale for the removal of iron from sulphuric acid leaches of sintered beryl[1], the extracting agent here being thiocyanate and the solvent methyl isobutyl ketone. The production of ultra-pure beryllium oxide is the purpose of another process[7] in which a solution of beryllium acetylacetonate in carbon tetrachloride is purified by extracting the other metals from it with an aqueous solution of EDTA. This process of course is not intended for the processing of ores, but only for the terminal purification of previously extracted beryllium oxide.

Neither of these processes is at present in large scale use.

The only other solvent extraction processes for beryllium are those previously described (Chapter III, section 2). They are used only in analysis or theoretical investigations.

Section 3: EXPERIMENTAL

Most of the experimental details of this chapter are given in the preceding two chapters, or, in what seemed a more natural place for them, with the results and discussion. Analysis here was usually by the Morin method. The complete analysis of the "Anaconda" betrandite and the qualitative analysis of the ore leach for all metals were carried out by x-ray emission spectroscopy by Mr. Kenneth Ramlal of the Geology Department of the University of Manitoba.

Section 4: RESULTS AND DISCUSSION

The main study of ore leaching in this project was done on bertrandite ore obtained from the Topaz Mountain region of Utah. The beryllium content of this ore was found to be completely leachable with sulphuric acid. The ore did not have to be heat-treated nor even finely ground. One sample was ground to mesh 30, but another sample, when leached, had pieces ranging in size to 1 cm. In both the beryllium content was rendered completely water soluble with sulphuric acid as described below. The ore is very friable and porous.

The bertrandite ore on which most work was done, and to which the following will refer unless otherwise stated, was a sample obtained from the Anaconda Company. It was ground to 30 mesh and had the following composition:

BeO	0.88%
SiO_2	64.00%
Al_2O_3	10.70%
Fe_2O_3	1.24%
MgO	2.00%
CaO	8.10%
K_2O	2.85%
Na_2O	1.75%
MnO	0.57%
H_2O	7.50%

continued

F	3.16%
(O=F)*	-1.68%
	101.07%

The beryllium content of this ore was rendered completely water soluble by heating with 10 equivalents of sulphuric acid per equivalent of beryllium, that is 198 ml of concentrated sulphuric acid per kilogram of ore. Less than this could probably have been used but it is difficult to mix this small amount of acid with the ore and get all of the ore wet with acid, and this could, and on one occasion apparently did, cause incomplete leaching. Another ore which was about 2% beryllium oxide but of unknown overall composition was found to be completely leachable with five equivalents of sulphuric acid per equivalent of beryllium.

Heating was done in 1 or 2 l. beakers covered with clock glasses on hot plates whose surface temperatures were about 700°C. Heating usually continued 24 hours, although all reaction (except evolution of hydrogen fluoride) appeared to be complete in about 1 hour. The mixtures became dry and hard in about this time. Considerable HF comes off during heating, especially when larger amounts of acid are used. How much of the other metals are rendered soluble in this process has not been determined but a qualitative analysis of the leach has shown that in addition

* oxygen equivalent of fluorine

to beryllium, iron, aluminum, magnesium, calcium, sodium, potassium and manganese are released. A good deal of acid remains in the ore and passes into the aqueous solution.

After heating, water was added, the cake broken up, and the mixture kept near boiling for 2 - 4 hours. This long heating was considered necessary to assure the hydration and solution of any anhydrous beryllium sulphate formed during the heating with sulphuric acid.

The leached ore consists of brown and black "sand" unchanged in appearance from the original, and a fine white solid which is probably calcium sulphate. The solid is removed by filtration with suction and washed several times with hot water.

Completeness of leaching was checked by making up the resulting solution to a known volume, analyzing for beryllium concentration, and comparing this with the concentration expected from the weight of ore used. The ore was analyzed by taking the beryllium into solution with sulphuric and hydrofluoric acids and determining its amount by the morin or zenia method.

The consistency of the results, indicating complete leaching, shows that, as might be expected, no fluoride entered the leach solution. Fluoride would certainly cause low beryllium analysis by either of the above methods.

Of the metals in the ore rendered soluble by sulphuric acid leaching iron, aluminum, and manganese need concern one in attempting to obtain pure beryllium. Manganese and aluminum have about the same distribution coefficients into conditioned MIK, and hence any system set up for the removal of one in the extraction stages will remove the other.

Under any circumstances where beryllium would extract approximately 100 percent iron, in either of its oxidation states, would extract likewise. Therefore separation of the beryllium from the iron could be accomplished in the extraction step only if sequestering agents were added to keep the iron in the aqueous phase, EDTA would be useful for this. However, as was stated, it was considered that the use of such expensive reagents was to be avoided if possible. Two methods of removing the iron which do not use sequestering agents are suggested.

(1) Extraction of the acid solution from the leaching step with a solution of thiocyanic acid in an organic solvent, probably MIK. Since the aqueous solution is highly acidic and no thiocyanate is added to it, loss of beryllium to the organic phase would be negligible. Iron III thiocyanate however is readily extracted under such circumstances. This method was tested as follows:

aqueous solution (initial) 0.08 M Be^{+2}

0.05 M Fe^{+3}

0.05 M H_2SO_4

MlK solution: 4 M HSCN

60 ml of the aqueous solution were extracted five times with 20 ml lots of the MlK solution. At the end of these extractions the beryllium content was unchanged but the iron concentration (as determined by visual colourimetry of $FeSCN^{++}$ in Nessler's tubes) was reduced to 0.0001 M.

Thus the iron concentration of the leach solution, before its excess acid is neutralized, could be reduced to any desired level by countercurrent extraction with an MlK solution of thiocyanic acid. The MlK solution of thiocyanic acid could be part of that from the thiocyanate recovery step. Alternatively, part of the excess acid in the leach solution could be removed by adding ammonium thiocyanate to it and extracting this and the iron with MlK. If the aqueous solution is left with pH $<$ 0.3 no beryllium will extract.

The solvent from extraction of iron by this method could be purified for re-use by washing with aqueous ammonia. Both iron and thiocyanate would be removed. If desired, this aqueous solution could then be filtered and the solution of ammonium thiocyanate used again in the extraction.

(2) If the iron is not removed before the extraction of the ore leach it could be removed from the solution of beryllium and iron obtained by stripping the extract, by taking advantage of the fact that beryllium is amphoteric and iron is not. The metals would be precipitated as the hydroxides and filtered off, the aqueous ammonium thiocyanate solution sent back into the extraction system, and the cake of hydroxides reacted with an excess of sodium hydroxide solution. Beryllium would dissolve as the beryllate and the iron hydroxide could be filtered off. Beryllium hydroxide would then be reprecipitated by passing in carbon dioxide to neutralize the excess alkali.

It seems probable that the last method would be the most economic because the process in which beryllium hydroxide is redissolved with excess alkali and reprecipitated with carbon dioxide is already used in beryllium production to obtain "high density" beryllium oxide. This step in the process could thus be made to serve two purposes. However if the ore leach contained a large amount of iron it might be advantageous to reduce its amount by such a process as (1) before beginning the beryllium extraction.

The leach solution, with or without its iron, must be brought to the correct pH and thiocyanate concentration before extraction can commence. It has been suggested that the excess acid be neutralized with lime.

This would be cheap, but if ammonia is used to neutralize the acid most of the aluminum would be removed from the solution as alum ($NH_4\ Al(SO_4)_2 \cdot 12H_2O$) at this point and more would come out in the same way (because the sulphate concentration would remain high) when the ammonium thiocyanate is added. Also, as will be shown later, the presence of a high sulphate content increases the separation factor of beryllium from aluminum in the MIK extraction. The question of the best neutralizer is again a matter of economics.

In the laboratory, where ammonia was always used to neutralize the excess acid, the alum was found to come out of solution as large clear crystals which carried no beryllium. However their formation was slow, and several days had to elapse before crystallization of alum ceased and the solution could be used in extraction.

Final adjustment of the pH would have to wait until the alum had ceased to come out of solution. The conditioned MIK has considerable "buffering" power but the aqueous solution would still have to be brought to a pH within a rather narrow range (1.5 to 3.5).

Countercurrent extraction would then be carried out using conditioned MIK in some type of extraction apparatus. Setting up the optimum conditions for such an extraction would require extensive calculations and pilot plant work, especially if two solvent extraction was intended, as it probably would be.

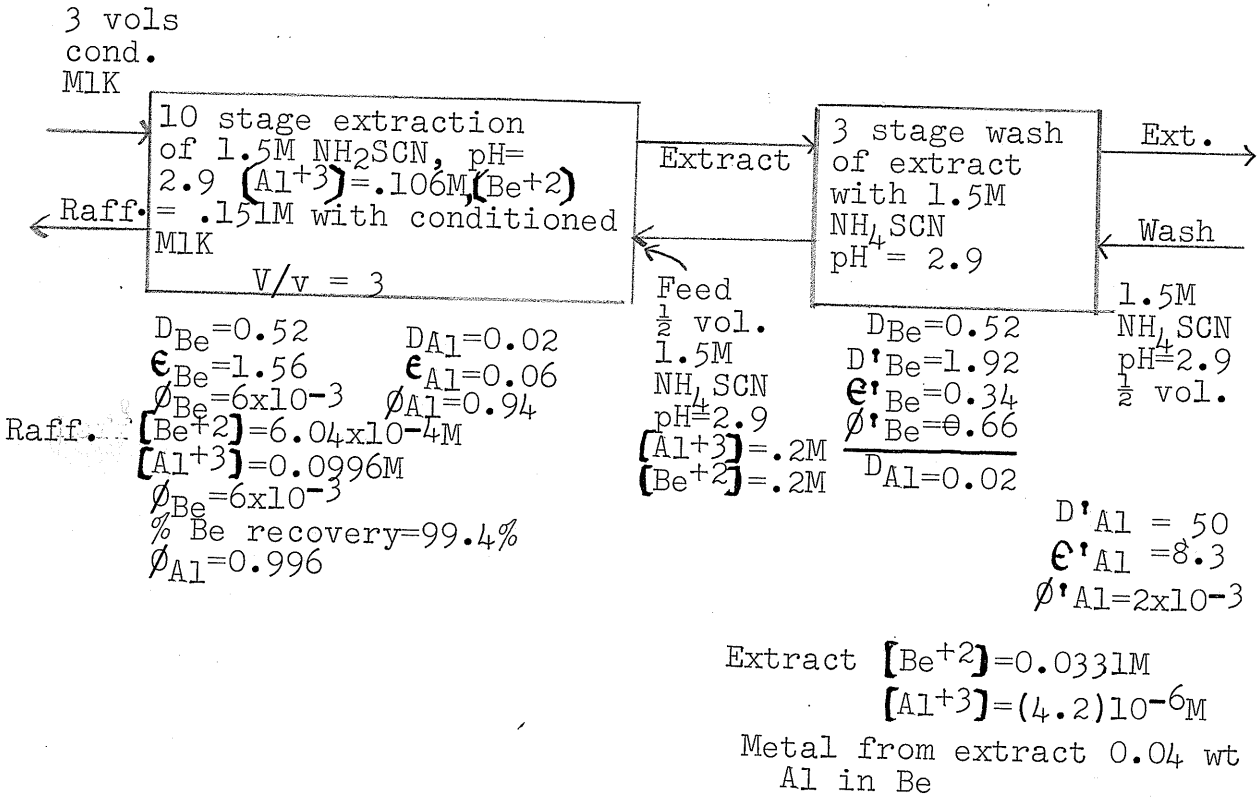
It has been shown that the distribution coefficient of beryllium thiocyanate is unaffected by the beryllium concentration, and hence, if sufficient stages are used, complete extraction of beryllium can be achieved if $\epsilon_{Be} \geq 1$. The only factor changing the distribution coefficient from stage to stage would be the change of thiocyanate concentration with extraction of the metals, which would be considerable at the high concentrations of the ore leach solution.

This too would be the only factor affecting the distribution coefficient of aluminum from stage to stage in the extract stages unless one were using the system for the further purification of a sample of beryllium of very low aluminum content.

A factor affecting the distribution coefficients which has been discovered in the course of this work is the sulphate concentration. Because the sulphate ion complexes both beryllium and aluminum, it lowers the distribution coefficients of their thiocyanates, but it was found to lower D_{Al} more than D_{Be}, increasing the separation factor β Be/Al = D_{Be}/D_{Al}. This is obviously advantageous in obtaining a separation of beryllium from aluminum, but it adds another complication to the extraction system which must be taken into account in any calculations.

As pointed out, there is a limit to the purity of extract one can obtain by simple countercurrent extraction imposed by the separation factor β, and the necessity of having ϵ_{Be} (in this case) ≥ 1 in order to obtain complete recovery of beryllium from the aqueous leach. This limitation can be circumvented by the use of two solvent extraction. In this case this would mean setting up a system such as the following. The figures given are typical of what one might encounter in this extraction. Calculations are shown in Appendix 2.

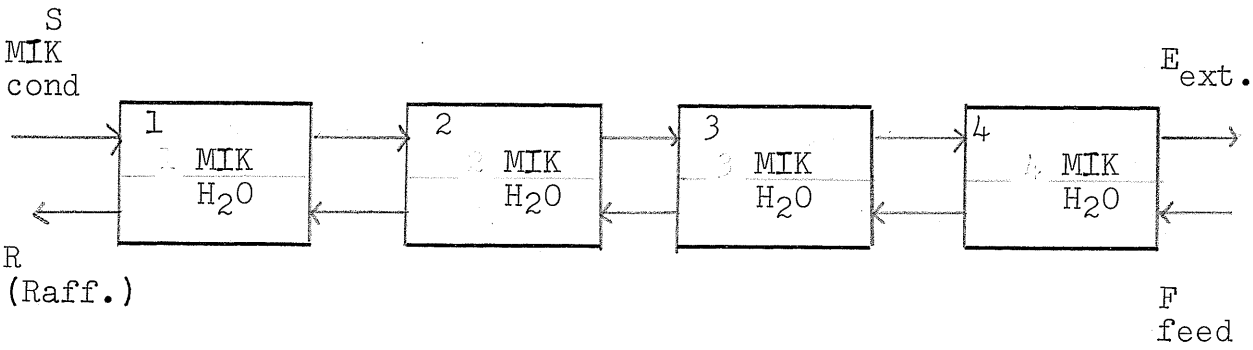
The wash carries some of the beryllium and almost all of the aluminum in the extract back into the extract stages. There the beryllium is returned to the extract. If the distribution coefficients were unaffected by metal concentration there is no limit, in principle, to the purity of the beryllium that could be obtained by this method. However, as previously shown, the distribution coefficient of aluminum increases after the aluminum concentration drops below 0.0025 M. This means that in the wash stages D'_{Al} and hence ϵ'_{Al} is decreasing from stage to stage toward the extract exit end. If ϵ'_{Al} eventually reaches a value less than 1 there is a limit to the amount of aluminum which can be washed out of the extract in these stages. This of course could be partly offset by



using large volumes of wash, and it might be circumvented entirely by using complexing agents in the wash to remove aluminum. A few studies of countercurrent extractions were undertaken and they indicate the type of results which can be expected. The system of separatory funnels illustrated by Alders[38], page 116 and in Fig. 14, page 192, was used. In such a manual process losses, evaporation, and entrainment take place in every transfer, and in addition to this the error in analysis (by Morin) can be doubled in the calculation of the distribution coefficient. But the results accord very well with predictions from the

Kremser Equation when the average distribution coefficient is used in the calculations.

The following diagram of the four-stage countercurrent run of Table XXXI shows the numbering of stages used in this and other runs. A cycle is a single movement of the liquids as indicated by the arrows.



In all countercurrent runs shown the solvent was conditioned MIK, and the aqueous feed, besides having the concentrations shown, was saturated with methylisobutyl ketone. Analysis for thiocyanate where carried out was by titration with standardized mercury (II) solution.

Table XXXI shows the 4 stage extraction of an aqueous solution of beryllium and aluminum. Table XXXII shows the 10 stage extraction of the same. The 10 stage extraction could be carried out at about 4 cycles per hour.

In addition to these, a ten stage extraction of an ore leach solution was carried out. An aqueous solution from leaching of the "Anaconda" bertrandite had been prepared which was approximately 0.12M in beryllium. It had most of its iron removed by extraction with thiocyanic acid

in MIK, and its pH had been adjusted to approximately 3. 1500 ml of this were mixed with 500 ml of 8M ammonium thiocyanate. The alum was allowed to settle out (taking several days) the solution saturated with MIK (only 7 ml of MIK per liter of solution were required to saturate this solution, as compared to 25 ml/l of pure water) and a final adjustment of pH to 2.9 made. This aqueous solution was then extracted with conditioned MIK in a ten stage countercurrent system of separatory funnels. Only the initial and final solutions were analyzed, the beryllium by the morin method, the aluminum by oxine. The data on this extraction were:

Initial aqueous solution: $[Be^{+2}] = 0.088M$

$[Al^{+3}] = 0.080M$

$[NH_4SCN] = 2.10M$

Solvent: Conditioned MIK

Volume ratio: V/v = 3

Cycles: 40

Raffinate:

$[Be^{+2}] = 6 \times 10^{-6}$ M

$[Al^{+3}]$: doubtful. Finely divided precipitate of alum made analysis difficult. Agitation and precipitate of sulphur from thiocyanate seems to increase the precipitation of this and to make it nearly colloidal. The value of $\emptyset Al$ below is obtained from the Al^{+3} concentration of the original aqueous solution and the extract.

Extract: $[Be^{+2}] = 0.028$ M

$[Al^{+3}] = 5 \times 10^{-4}$ M

$\therefore$ Al_2O_3 in BeO from extract would constitute 3.5 percent by weight.

D_{Be} and D_{Al} were determined for extraction of the metals by conditioned MIK from this solution:

$D_{Be} = 0.83$

$D_{Al} = 0.0055$

$\beta_{Be/Al} = 151$

The values where the aqueous solution contains only ammonium thiocyanate and the beryllium or aluminum salt are:

$D_{Be} = 1.20$

$D_{Al} = 0.05$

$\beta_{Be/Al} = 25$

The effect of sulphate can be seen. From the values of D_{Be}, D_{Al}, and V/v the fractions of the metals not extracted were predicted to be:

$\phi_{Be} = 6 \times 10^{-5}$

$\phi_{Al} = 0.98$

Those found were:

$\phi_{Be} = 6.8 \times 10^{-5}$

$\phi_{Al} = 0.99$

The treatment of the extract after the extraction would depend somewhat on whether the iron had been removed before extraction began. Stripping the extract would probably best be done with a dilute solution of sulphuric acid. If no iron is present in the extract the beryllium could be precipitated at once from this solution with ammonia, filtered off and ignited. Its treatment if iron is present has already been discussed. Since the strippings after precipitation of the metals would contain about half the ammonium thiocyanate used in the extraction step it would be returned to the incoming leach. Here, as in the recovery from the raffinate step, no concentrating of the solution would be required if the volume of solution used in stripping is kept sufficiently low and the concentration of aqueous ammonia used in the precipitation sufficiently high.

The stripped MIK from the extract would be used in recovery of the thiocyanate from the raffinate, or returned to the extraction after conditioning. The thiocyanate in the raffinate would be recovered by acidifying with sulphuric acid until $[H_2SO_4] \simeq [SCN^-]$, and extracting with MIK. The thiocyanate extract in MIK would then be stripped with concentrated aqueous ammonia and the resulting aqueous solution of ammonium thiocyanate returned to the incoming leach solution. Loss of thiocyanate in the extract

and recovery stages, probably amounting to only a few percent of that used per cycle, would be made up with new ammonium thiocyanate.

The MIK would probably never need distilling. The only impurities it would be likely to pick up would be decomposition products of thiocyanate and these would probably be harmless, present in small amount, and not apt to accummulate. However losses might amount to several percent per cycle due to its aqueous solubility.

The flow scheme which follows is based on the above results, and speculations. Notes following it explain the calculations, assumptions and approximations on which individual parts are based. Whether the main extraction step utilizes one solvent extraction or two would not substantially affect the quantities here calculated. Two solvent extraction is obviously called for if the beryllium oxide produced is to be better than about 96 percent pure. Single solvent extraction is here assumed to simplify calculations.

Fig. 14

This is the operation or flow pattern for single solvent countercurrent extraction in 10 stages using 5 separatory funnels (represented by squares).

Repetition of the transfers of the last two "layers" (within dotted lines) accomplishes continuous countercurrent flow through ten stages such as shown at bottom. The different liquids flowing in the system are indicated by letters:

F - feed

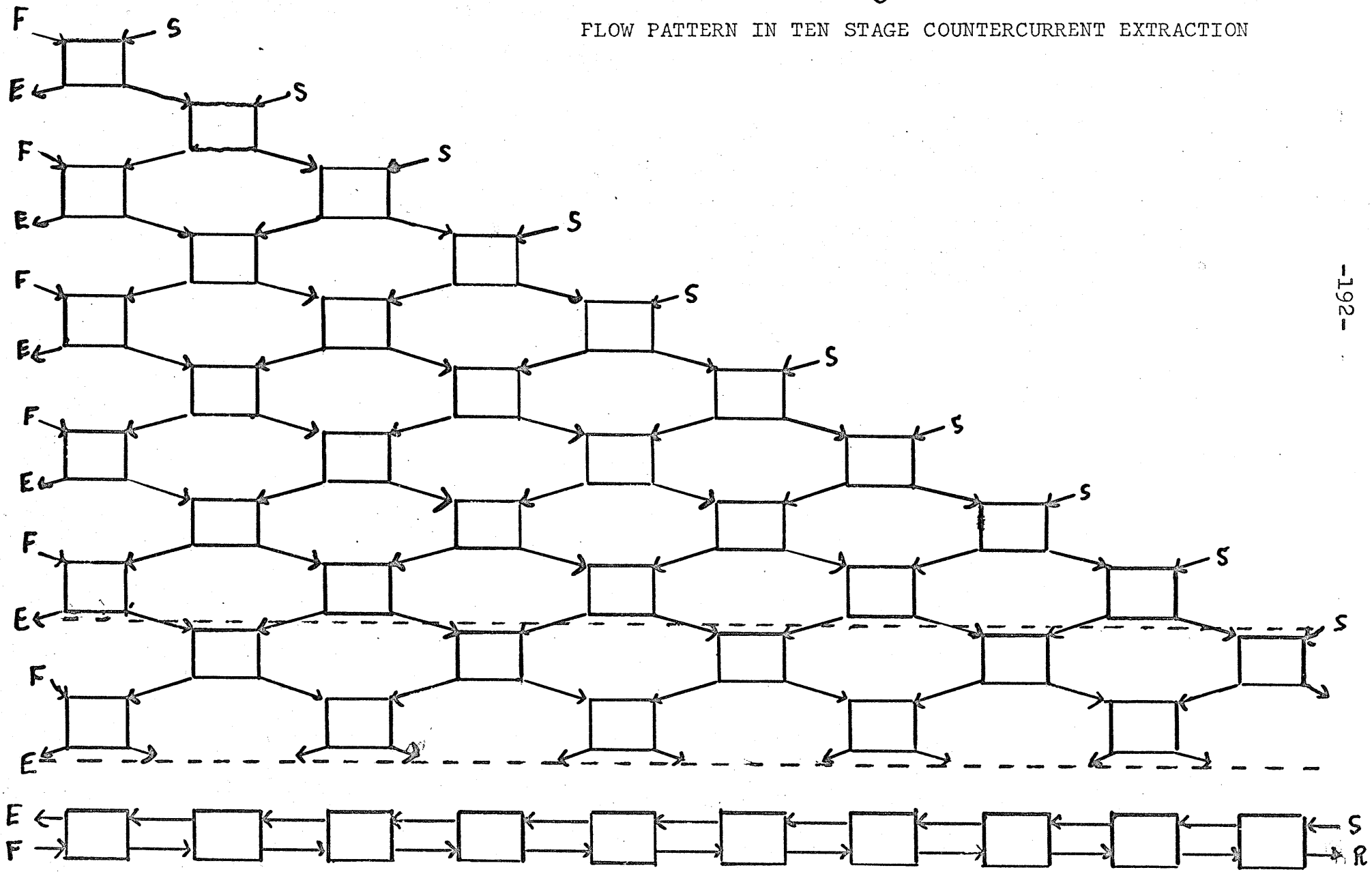
E - extract

S - solvent

R - raffinate

Fig. 14

FLOW PATTERN IN TEN STAGE COUNTERCURRENT EXTRACTION



TABLES XXXI and XXXII

These tables show the results of countercurrent extraction of aqueous solutions of beryllium sulphate, aluminum nitrate, and ammonium thiocyanate with conditioned MIK. Conventions and symbols used in these tables are the same as used in previous tables.

TABLE XXXI

4-Stage Countercurrent Extraction

Conditions: stages: 4

V/v = 1.5

cycles: 24

Feed (initial aqueous solution): $(BeSO_4)$ = 0.10 M

$(Al(NO_3)_3)$ = 0.10 M

(NH_4SCN) = 1.5 M

pH= 2.90

Solvent: conditioned MIK

Analysis: SCN^- - Hg^{+2} titration

Be - zenia

Al - oxine

No.	pH	(SCN^-)	(Be^{+2})	(Al^{+3})	D_{Be}	D_{Al}
1 aq.	2.75	1.397	0.023	0.088	0.65	0.021
1 org.			0.015	0.019		
2 aq.	2.81	1.408	0.046	0.088	0.63	0.017
2 org.			0.029	0.0015		
3 aq.	2.80	1.446	0.061	0.086	0.71	0.021
3 org.			0.043	0.0018		
4 aq.	2.80	1.482	0.083	0.086	0.66	0.025
4 org.			0.055	0.0022		
orig. aq.	2.78	1.503	0.118	0.086		
			0.00	0.00		
orig. org.			0.00	0.00		

Table XXXI continued,

average: $D_{Al} = 0.021$

" $D_{Be} = 0.66$

Whence predicted: $\phi_{Al} = 0.98$

$\phi_{Be} = 0.20$

Found: $\phi_{Al} = 0.98$

$\phi_{Be} = 0.20$

10-Stage Countercurrent Extraction

Conditions: stages: 10 Feed: $(BeSO_4)$ = 0.10 M

V/v = 3 $(Al\ NO_3)_3)$ = 0.10 M

cycles: 40 (NH_4SCN) = 1.5 M

solvent: conditioned MIK pH = 2.90

analysis: Be: morin SCN^-: Hg^{+2} titration

Al: oxine

No.	pH	(SCN^-)	(Be^{+2})	(Al^{+3})	D_{Be}	D_{Al}
orig. aq.	2.66	1.496	0.095	0.096		
orig. org.			0.00	0.00		
1 aq.	2.68	1.338	0.00036	0.093	0.39	0.028
1 org.			0.00014	0.0026		
2 aq.	2.67	1.333	0.0010	0.093	0.57	0.034
2 org.			0.00059	0.0032		
3 aq.	2.68	1.333	0.0019	0.092	0.55	0.031
3 org.			0.0011	0.0029		
4 aq.	2.68	1.336	0.0036	0.095	0.66	0.032
4 org.			0.0024	0.0031		
5 aq.	2.70	1.337	0.0063	0.095	0.57	0.26
5 org.			0.0036	0.0025		
6 aq.	2.70	1.334	0.014	0.084	0.37	0.033
6 org.			0.0054	0.0028		
7 aq.	2.70	1.343	0.015	0.090	0.85	0.026
7 org.			0.013	0.0024		
8 aq.	2.70	1.354	0.026	0.088	0.60	0.020
8 org.			0.014	0.0018		
9 aq.	2.73	1.369	0.042	0.088	0.53	0.034
9 org.			0.022	0.0030		
10 aq.	2.74	1.420	0.065	0.086	0.63	0.039
10 org.			0.041	0.0034		

Table XXXII continued,

Average $D_{Al} = 0.030$

$D_{Be} = 0.57$

Whence predicted: $\phi_{Al} = 0.91$

$\phi_{Be} = 0.002$

Found $\phi_{Al} = 0.97$

$\phi_{Be} = 0.004$

Fig. 15

This is the flow scheme for the extraction of beryllium oxide from acid leachable bertrandite ore by the solvent extraction of beryllium thiocyanate.

Numbers in brackets refer to notes on pages following.

Fig. 15

FLOW SCHEME FOR EXTRACTION OF BERYLLIUM FROM BERTRANDITE ORES

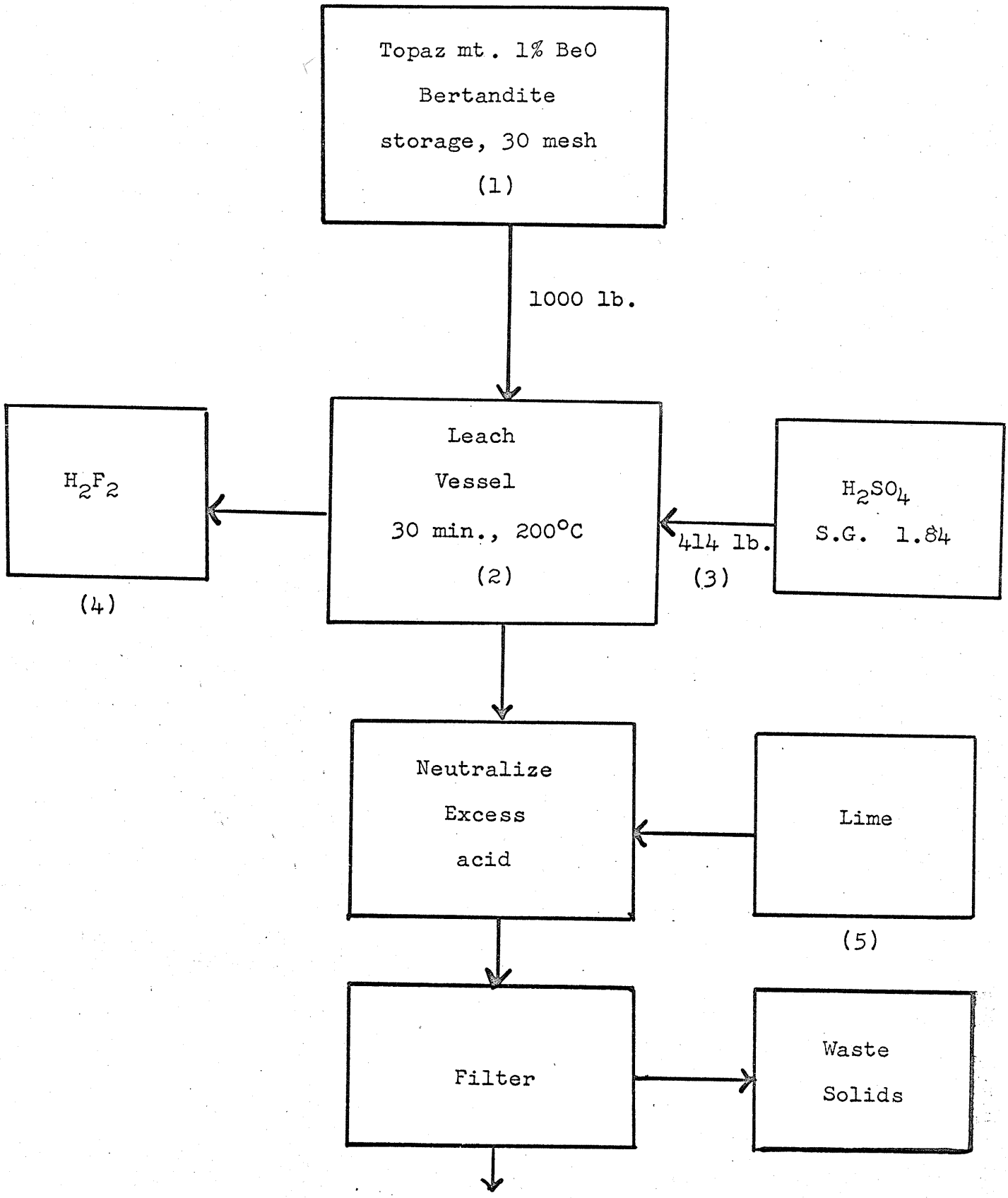
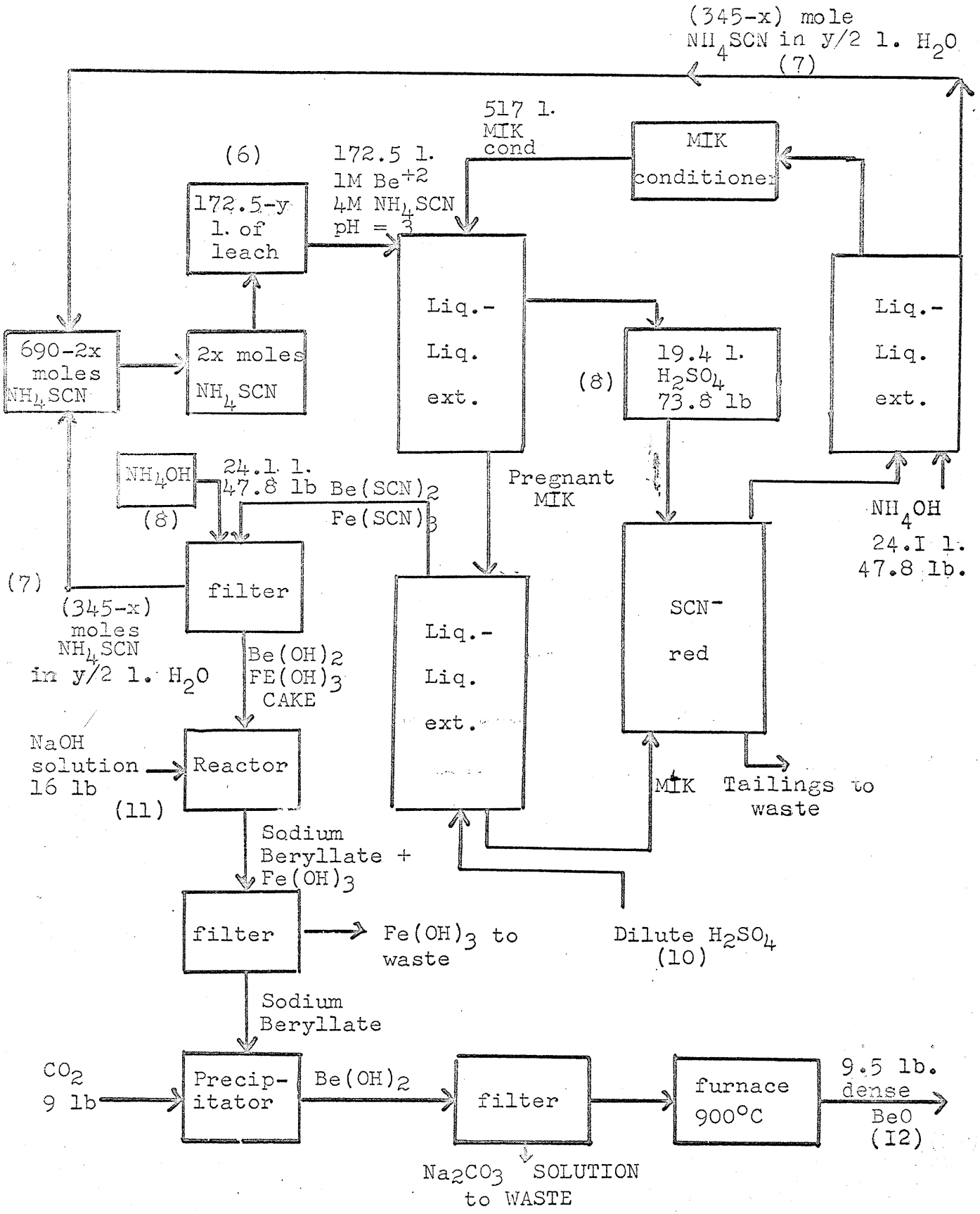


Fig. 15 continued,



Notes on Flow Sheet

1. Ore containing 1 percent of beryllium oxide is chosen as the starting point since such an ore is typical of the acid leachable Topaz Mountain deposits. A higher grade ore might permit reduction of the amount of sulphuric acid required in the leaching step; a lower grade ore might require more sulphuric acid. This is the only effect the grade of the ore is likely to have on the particulars of this flow sheet.

2. Conditions of time and temperature in the leaching step have still to be optimized. Those given would be suitable.

3. The question of the amount of sulphuric acid called for has already been discussed. The amount given here was calculated to give ten equivalents of sulphuric acid per equivalent of beryllium in the ore, which is certainly sufficient for those ores which were here studied.

4. The hydrogen fluoride produced could be converted to ammonium fluoride and used in the production of beryllium metal in an integrated process. Alternatively it could be a valuable by-product. The amount of fluorite in Topaz ores is substantial.

5. The question of the possible methods for neutralizing the excess acid has been discussed on page 182.

6. An advantage is gained if the feed to the extractor is as concentrated in beryllium as circumstances will permit, for then the extraction is carried out with the smallest possible amounts of MIK and ammonium thiocyanate and the losses of these per unit of beryllium oxide produced are similarly minimized. The volumes given here are calculated to make the initial feed (containing 9.5 pounds of beryllium oxide) 1M in beryllium and to give the raffinate a thiocyanate concentration of 2M.

7. Recovery of thiocyanate in these stages could probably be made better than 95 percent. On the assumption that the overall recovery of thiocyanate is 90 percent $x = 34.5$ moles and $2x = 11.5$ pounds of ammonium thiocyanate. This is the amount of ammonium thiocyanate which will have to be added per 1000 pounds of ore processed. The ammonium thiocyanate solutions leaving each recovery stage should be as concentrated as possible in order to keep the volumes entering the extractor low. If heat is used to keep the salt in solution the concentrations could approach that of concentrated aqueous ammonia (14.3M). It is assumed here that no concentration by evaporation is necessary.

8. The volumes of sulphuric acid and ammonia entering the recovery stages are calculated on the assumption that recovery of thiocyanate is 100 percent and that beryllium is 100 percent extracted. No other metals are assumed to be present in the extract. The amount of sulphuric acid used in the recovery of thioycanate is calculated to give 1 mole of sulphuric acid per mole of thiocyanate.

9. The flow sheet assumes no losses of MIK.

10. Dilute sulphuric acid(probably about 0.1 M would be satisfactory) is used rather than water in stripping the extract to prevent the formation of a stable MIK in water emulsion.

11. Reaction of the precipitated hydroxides with excess sodium hydroxides followed by filtering and reprecipitation of beryllium with carbon dioxide removes any iron in the extract (as the hydroxide in filtering) and produces "high density" beryllium hydroxide in the precipitation from homogeneous solution. See page 182.

12. Production of 9.5 pounds of beryllium oxide from 1000 pounds of this ore assumes 95 percent recovery. It is probable that recovery would be at least this high.

An estimate of the cost of producing one pound of beryllium oxide for chemicals and operating expenses can now be made. If the system is run as shown, these are:

Sulphuric acid, approx. 500 lbs. at $25/ton	$6.25
Ammonia, approx. 100 lbs. at $92/ton	$4.60
Sodium hydroxide, 16 lbs at $10/cwt.	$1.60
Ammonium thiocyanate, 11.5 lbs. at $21/cwt	$2.42
Methyl isobutyl ketone, 3 gal. (assuming loss of approx. 2.5%) at $0.20/gal.	$0.60
Carbon dioxide, 9 lbs. at $0.08/lb.	$0.72
Labour (estimated)	$5.00
Electric power & natural gas (estimated)	$2.50
Total cost per 9.5 lbs. BeO	$23.69
Cost per pound of BeO	$2.49

Chemical and Engineering News, Quarterly Report on Current Prices October 29, 1963, gives the price of beryllium oxide as $12.50 to $15.00 per pound, the variation presumably reflecting purity.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The critera for a satisfaxtory extraction system for the production of beryllium from its ores have been well met in the system using ammonium thiocyanate as the extracting agent and methyl isobutyl ketone as the solvent. Although it cannot yet be stated what purity of beryllium oxide could be produced by this method in its simple form (i.e., without sequestering agents such as EDTA) it is obvious from the calculations of appendix 2 that beryllium oxide could be produced by this method in a state of purity exceeding that attained by the other two processes of large scale beryllium production. Normally the beryllium oxide appearing on the market contains a few tenths of a percent of impurities, chiefly iron and aluminum. It has been shown by the above mentioned calculations that the present system would be able to reduce these contaminants in the beryllium oxide at least to a few hundreds of one percent.

Thus this system has the selectivity for beryllium demanded. Also it does not use expensive reagents or solvents. The solvent and thiocyanate are both easily recoverable with only small losses expected.

The major cause of loss of solvent would arise from its solubility in the aqueous phases during extraction, but even if the aqueous phase were pure water this solubility only amounts to about 25 ml per liter. The losses of solvent arising from its aqueous solubility would be reduced by the high concentrations of salts sometimes in the aqueous phase and by the volume ratioes $\frac{V_{MIK}}{V_{H_2O}}$ which are always greater than unity in the extraction steps.

Thiocyanate would be lost mainly through decomposition, or through incomplete extraction in the recovery stage. Since the time for a single cycle in the extraction system can be kept short it is unlikely that the first cause would result in a large loss percentage-wise. Thiocyanate is quite stable in solution when acid is not present, and in this system it would be in acid solution only in the recovery stage.

Recovery of thiocyanate by the system contemplated would probably be greater than 95 percent complete. It was shown that even in a single batch-wise extraction under the conditions planned for the recovery stage 94 percent of the thiocyanate was extracted.

Other reagents have been assumed to be unrecoverable in computing the cost of raagents needed in this process. Also the possibility of valuable by-products such as hydrofluoric acid has been ignored, although in one beryllium

oxide production method the hydrofluoric acid also produced was expected to bear half the cost of the process. The cost per pound of beryllium oxide is still low compared to its market price of $12.50 to $15.00 per pound.

This process obviously has the advantage of being a continuous rather than a batchwise process. It also promises to be more flexible and amenable to modification for changed conditions of use than are the present systems. What the cost of equipment and operation would be cannot at present be said, but there is no reason to believe they would be great. High temperatures are called for only to sinter the beryllium oxide produced, and the only corrosive material entering the system, sulphuric acid, is used in small amount.

Whether or not this system could be used to produce ultra-pure beryllium oxide depends on the behaviour of the distribution coefficient of aluminum at low concentrations, or on whether the use of agents such as EDTA to sequester the aluminum would be economically feasible. If the distribution coefficient of aluminum does not increase sufficiently with decreasing aluminum concentration to drive ϵ'_{Al} below unity in the wash stages of a system then there is, in principle, no limit to the purity of beryllium oxide which could be produced. (This statement of course assumes that aluminum is the only impurity of consequence.) If D_{Al} does

continue to rise as the data of Table XV indicate there may be a practical limit of purity with respect to aluminum contamination which cannot be passed unless masking agents such as EDTA are added to hold the aluminum in the aqueous phase.

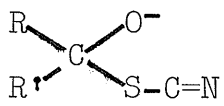
Further speculation on the behaviour of this system in large scale operation would not be justifiable at present. Enough data have been obtained however to show that, as a method for obtaining relatively pure beryllium oxide from low grade bertrandite ores the solvent extraction system using thiocyanate and methyl isobutyl ketone is very promising. The next step is pilot plant operation and large scale testing of such steps in the process as ore leaching, reagent recovery, and iron removal. It is hoped that this work can begin soon.

The other aspect of this research, the investigation of the chemistry of the thiocyanate extraction system, has likewise yielded a clear and detailed picture of the chemical species involved. It was shown that the metals aluminum, beryllium, manganese (II) and iron (II), and perhaps iron (III) and lithium extract from aqueous thiocyanate containing solutions into organic solvents as their thiocyanate salts.

Beryllium and aluminum extract from these aqueous solutions as hydrated cations and the water molecules of

their hydration spheres give rise to many absorption bands in the near infra red. The study of these absorption bands, coupled with Karl Fisher determinations of the water content of the MIK extracts revealed the nature of the extracted aluminum and beryllium species in detail. Both cations normally extract with their full hydration sphere, that is, all the coördination positions about the extracted cations are filled by water molecules. The beryllium ion also carries some water molecules outside of its primary hydration sphere. Like all water in these solvents the water of the hydration spheres of these cations is hydrogen-bonded to the oxygen atoms of the solvent molecules. In the case of beryllium polymerization of the extracted species through the water molecules occurs as the concentration of the beryllium in the extract increases, leading to less hydrated species.

The thiocyanate ion is strongly solvated by alcohols, ketones and esters. In ketones it forms a species having the structure



Water molecules in the ketone are bound by hydrogen bonds to the oxygen or the triple carbon-nitrogen of this species.

Where the extracting salt is beryllium thiocyanate the ketone-thiocyanate species is strongly hydrogen-bonded to the water molecules of the hydration sphere of the beryllium ion. In the extracts of aluminum thiocyanate however the ketone-thiocyanate species is bound to water molecules which are not part of the hydration sphere of the aluminum ion. The result of this is that in beryllium extractions only the beryllium ion carries water into the extract while in aluminum extractions both the aluminum ion and the thiocyanate ion carry water into the ketone phase. The concentration of "free water" (water bound only by solvent and thiocyanate) in the extracts increases with the aluminum concentration of the extracts but not with the beryllium concentration.

The beryllium thiocyanate species extracting into methyl isobutyl ketone is shown on page 164, the aluminum thiocyanate species in the same solvent on page 165.

The extraction of ammonium thiocyanate into organic solvents is enhanced by the presence of thiocyanic acid in the solvent. To account for this it is postulated that the solvent-thiocyanic acid species can form hydrogen bonds to the triple bond of the thiocyanate ion thereby increasing the solubility of thiocyanate salts in the solvent. This is shown on page 161.

Although the solubility of ammonium thiocyanate in solvents such as methyl isobutyl ketone is increased by the presence of thiocyanic acid in the solvent the solubility of beryllium or aluminum thiocyanate appears to be decreased. This is probably due to the fact that the beryllium or aluminum ion must form an ion-pair or hydrogen-bonded group with the solvent-thiocyanate species in order to extract. The thiocyanic acid-solvent species, by itself hydrogen bonding to the thiocyanate ion, prevents the formation of such species with the beryllium or aluminum ions, i.e., the thiocyanic acid competes with the beryllium or aluminum for the thiocyanate ion, and thereby lowers their extraction in the solvent.

Beryllium and aluminum thiocyanate were shown to polymerize very extensively in their concentrated aqueous solution, and infra red spectra of their solids indicate the presence of bridging thiocyanate groups there also. The decrease of the distribution coefficient of aluminum thiocyanate with increasing concentration of the aluminum ion in the region 10^{-4}M to 10^{-2}M could be explained as due to polynucleation of the aluminum thiocyanate species in the aqueous phase. Polynucleation of aluminum thiocyanate in aqueous solution at these low concentrations is however considered unlikely and an alternative explanation of the observed phenomenon is offered. This is, that, as the

aluminum concentration in the organic phase decreases, the thiocyanate concentration there remaining relatively constant, the increasing of the thiocyanate-to-aluminum ratio causes polymerization in the organic phase. It is noted however that polymerization in the aqueous phase at concentrations of 10^{-5}M has been claimed to take place in indium bromide solutions[71] and indium bromide could be expected to have properties similar to those of aluminum thiocyanate, as respects polynucleation.

The different classes of organic solvents have been found to have widely differing powers to extract beryllium or aluminum thiocyanate from aqueous solutions, the order of increasing power being: mercaptans < ethers < esters < aldehydes ≤ ketones < alcohols. Hydrocarbons, halogenated hydrocarbons or fatty acids having no detectable extracting power. This is the order found elsewhere[55,83] except for the position of fatty acids which the work of Garwin and Hixson indicate should be one of the better extracting solvents. The inability of fatty acids to extract these salts is explained by their highly dimerized nature, which prevents them from forming hydrogen bonds to the thiocyanate or hydrated cations.

Data obtained in this work (page 114) indicate that thiocyanic acid is a strong acid, as found elsewhere[80,81]. Also Wood's value of the formation constant of the hydroxy

complex of beryllium[41] was used to calculate the free beryllium concentration at different pH's and hence to obtain the product $(Be^{+2})(SCN^{-})^{2}$. A plot of this product against E_{Be} gave the same straight line as was previously obtained for extractions at constant pH and varying thiocyanate concentration. This indicates the correctness of Wood's value of $K_{f_{BeOH^{+}}}$.

The work of this thesis may be divided into that of an applied or practical nature, developing a flow scheme for the separation of beryllium, and that concerned with the theory, mechanism, and chemistry of the thiocyanate extraction system. Both it is believed, have been carried to the point where definite conclusions can be drawn and the objectives set out in Chapter I have been satisfactorily achieved.

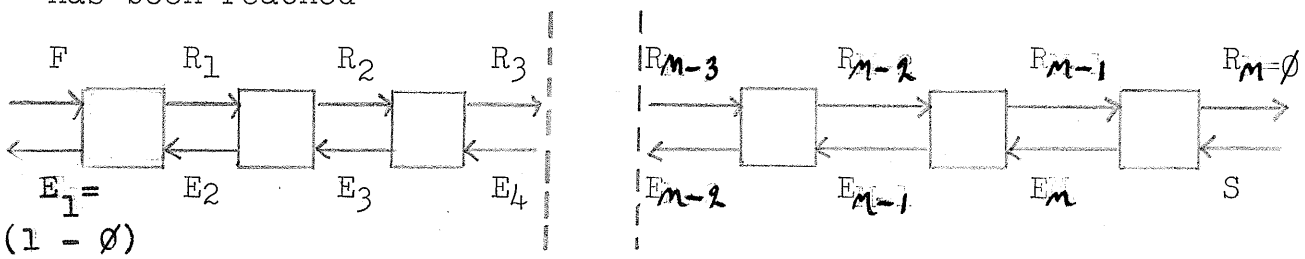
APPENDIX 1

DERIVATION OF THE KREMSER EQUATION[38]

A countercurrent extraction system of n stages is shown below. In this system a component X is being partitioned between the extract and raffinate phases of each stage according to the formula

$$\epsilon = \frac{\text{quantity of X in extract phase}}{\text{quantity of X in raffinate phase}}$$

ϵ being the extraction coefficient. Steady state operation has been reached



In a given time 1 part of component X is introduced into the feed end of the extraction system and Ø parts leave the system in the raffinate R_n. Hence there must be (1-Ø) parts of X leaving in the final extract E_1 in the same length of time. Let R and E refer to quantities. Then

$$R_n = \emptyset \qquad (2)$$

$$E_1 = 1-\emptyset \qquad (3)$$

From the definition of the extraction factor it follows that for each stage

$$E = \epsilon . R \qquad (4)$$

Hence, for stage n:

$$E_n = \epsilon . R_n = E.\phi \qquad (5)$$

and, from the material balance for stage n:

$$R_{n-1} + 0 = E_n + R_n \text{ or} \qquad (6)$$

$$R_{n-1} = \epsilon . \phi + \phi = \phi(\epsilon + 1) \qquad (7)$$

In stage n-1

$$E_{n-1} = \epsilon . R_{n-1} \qquad (8)$$

By substituting (7) we get

$$E_{n-1} = \phi(\epsilon^2 + \epsilon) \qquad (9)$$

From the material balance for stage n and n-1:

$$R_{n-2} + 0 = E_{n-1} + R_n \qquad)10)$$

and the substitution of equations (2) and (9) gives

$$R_{n-2} = \phi(\epsilon^2 + \epsilon + 1) \qquad (11)$$

and similarly for stage n-2

$$R_{n-3} = \phi(\epsilon^3 + \epsilon^2 + \epsilon + 1) \qquad (12)$$

Hence, for the second stage

$$R_1 = \phi(\epsilon^{n-1} + \epsilon^{n-2} + \epsilon^{n-3} + \cdots + 1) \qquad (13)$$

In stage 1

$$E_1 = \epsilon . R_1$$

By substituting equations (3) and (13) gives

$$1 - \phi = \phi(\epsilon^n + \epsilon^{n-1} + \epsilon^{n-2} + \text{-----} + \epsilon) \qquad (14)$$

Hence:

$$\frac{1 - \phi}{\phi} = \epsilon^n + \epsilon^{n-1} + \epsilon^{n-2} + \text{----} + \epsilon \qquad (15)$$

Giving $\frac{1}{\phi} = \epsilon^n + \epsilon^{n-1} + \epsilon^{n-2} + \text{----}\epsilon + 1$

$$= \frac{\epsilon^{n+1} - 1}{\epsilon - 1} \qquad (16)$$

Which is the Kremser equation

$$\phi = \frac{\epsilon - 1}{\epsilon^{n+1} - 1} \qquad (17)$$

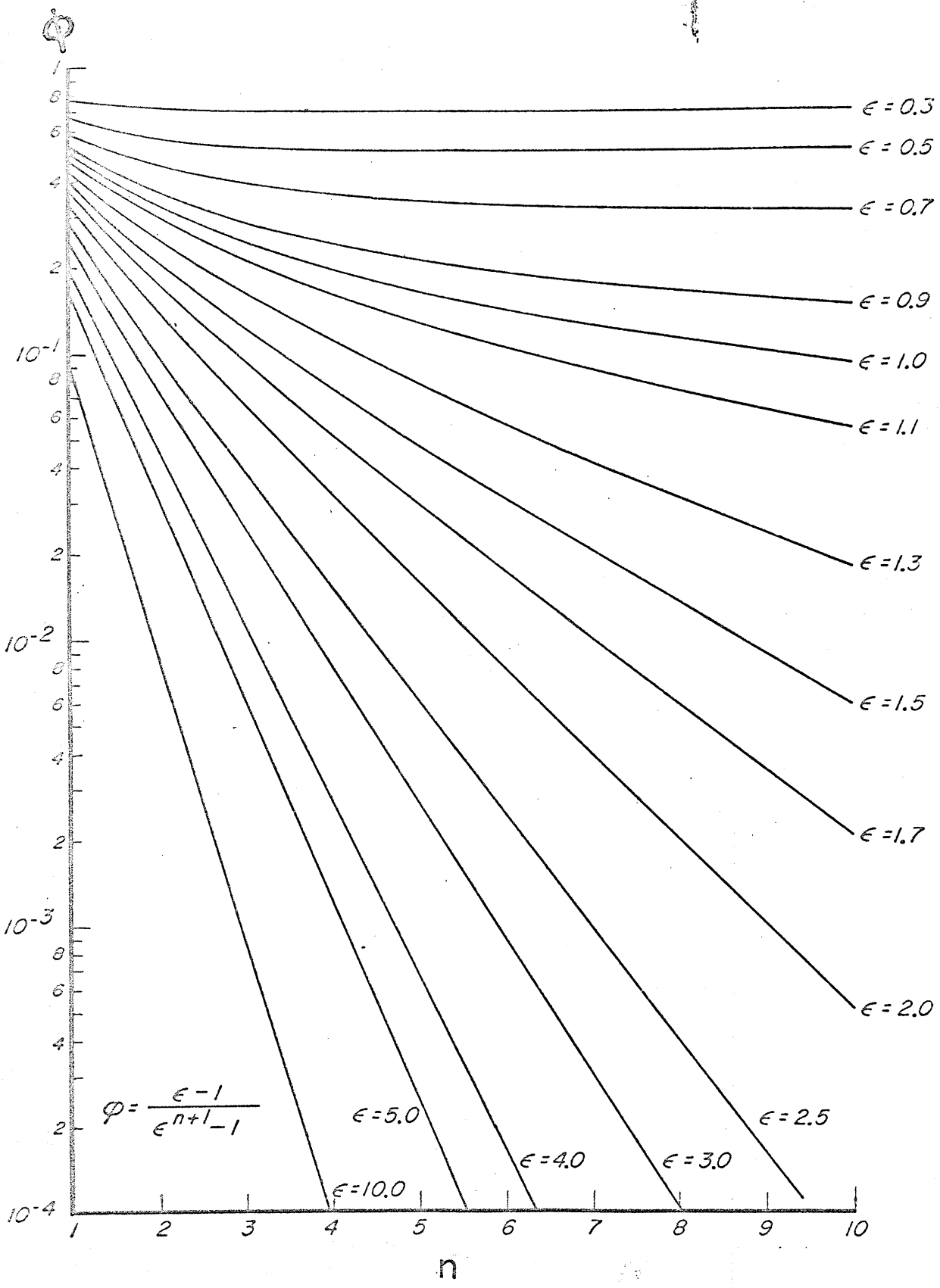
Fig. 16 shows plots of ϕ against n for different values of ϵ.

Fig. 16

Plots of the Kremser Equation.* These show the relation between the number of ideal stages (n) and the fraction of the extracting material not extracted (ϕ) in single solvent countercurrent extraction for different values of the extraction factor ϵ.

Reproduced from L. Alders,[38] "Liquid-Liquid Extraction", page 95.

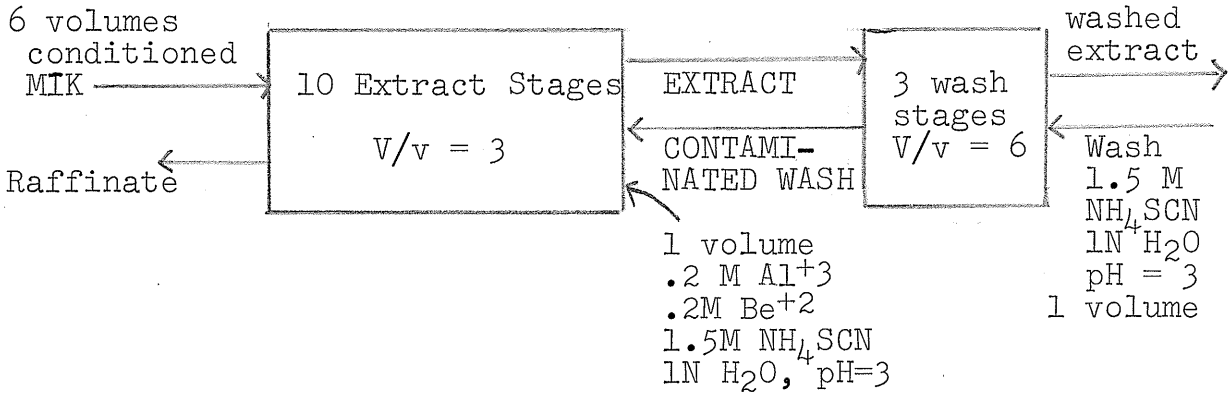
Fig 16


φ
1
8
6
4
2
10-1
8
6
4
2
10-2
8
6
4
2
10-3
8
6
4
2
10-4
1
2
3
4
5
6
7
8
9
10
n
ε = 0.3
ε = 0.5
ε = 0.7
ε = 0.9
ε = 1.0
ε = 1.1
ε = 1.3
ε = 1.5
ε = 1.7
ε = 2.0
ε = 2.5
ε = 3.0
ε = 4.0
ε = 5.0
ε = 10.0
φ = (ε − 1) / (ε^(n+1) − 1)

APPENDIX 2

An Example of Two-Solvent Countercurrent Extraction of an aqueous Solution of Beryllium, Aluminum, and Ammonium Thiocyanate with Conditioned Methyl Isobutyl Ketone.

The extraction system is as follows:



In these circumstances the distribution coefficients of the metals are:

$$D_{Be} = 0.52$$

$$D_{Al} = 0.02$$

The extraction factors in the extract and wash stages are then

Extract stages $\epsilon_{Be} = 1.50$

$\epsilon_{Al} = 0.06$

Wash stages $\epsilon_{Be} = 3.12$

$\epsilon_{Al} = 0.12$

In the wash stages it is back extraction, or extraction into the aqueous phase which is of interest. Hence it is the reciprocals of these extraction coefficients which are required there:

$$\epsilon'_{Be} = 0.34$$
$$\epsilon'_{Al} = 8.3$$

The problem is now to obtain the concentrations of the two metals in the final extract and raffinate in steady state operation by a method of successive approximations. The calculations which follow assume that the extraction coefficients of both metals are constant at all concentrations of the metals.

1st approximation: Extract stages. The extraction coefficients are as given above, and the concentration of both metals in the initial aqueous feed (1 volume of wash, 1 volume of feed 0.2M in both metals) is 0.1 M. From Fig. 16 the fractions of the metals left unextracted in the raffinate are read:

$$\phi_{Be} = 4 \times 10^{-3}$$
$$\phi_{Al} = 0.94 \quad \text{hence concentrations in the raffinate}$$

are:

$$(Be^{+2}) = (0,1)(4)(10^{-3})M = (4)(10^{-4})M$$
$$(Al^{+3}) = (0.1)(.94) = 0.094\ M$$

and in the extract $(Be^{+2}) = \frac{0.1}{3} = 0.0333\ M$

$$(Al^{+3}) = \frac{0.006}{3} = 0.002\ M$$

Dividing the concentrations in the extract by three takes into account dilution due to the volume ratio.

Wash stages: The extract with the above concentrations of beryllium and aluminum goes to the wash stages where the fractions of the metals left in the extract after passing through the three wash stages can be found from Fig. 16 and the above values of ϵ'_{Be} and ϵ'_{Al}:

$\phi'_{Be} = 0.66$

$\phi'_{Al} = (2)(10^{-3})$ Whence the

concentrations: washed extract

$$\left[Be^{+2}\right] = (.66)(.0333) = 0.0222 \text{ M}$$

$$\left[Al^{+3}\right] = (2)(10^{-3})(.002) = (4)\ 10^{-6} \text{ M}$$

contaminated wash

$$\left[Be^{+2}\right] = (.0333 - .0222)(6) = 0.0666 \text{ M}$$

$$\left[Al^{+3}\right] = (.002)(6) = .012 \text{ M}$$

Multiplication by six in the last two calculations again taking account of the volume ratio.

The wash with these concentrations of the metals enter the extract stages with the feed, and hence a new value for the concentrations in the feed can be calculated:

$$\left[Be^{+2}\right] = \frac{0.2}{2} + \frac{0.0666}{2} = 0.1333 \text{ M}$$

$$\left[Al^{+3}\right] = \frac{0.2}{2} + \frac{0.012}{2} = 0.106 \text{ M}$$

With these values for the concentration of metals in the initial aqueous feed the above calculations are repeated, giving a third value for the concentrations in the feed. This process of successive approximations is repeated until

the concentrations in the various solutions are not significantly changed by further repetition of the calculations. In this case a satisfactorily constant value for the aluminum concentrations was found after four approximations, a satisfactorily constant value for the beryllium concentrations after six. This is shown in Table XXXIII. The final values are those used in the example, page 186.

A purer extract, that is an extract with a higher ratio of beryllium to aluminum, could be obtained by using more wash stages. Since $\epsilon'_{Be} = 0.34$, which is less than unity any number of wash stages could be used without reducing the fraction of the beryllium left in the extract at the end of the wash stages to less than $\phi' = 1 - \epsilon'_{Be} = 0.66$. However the effectiveness of additional wash stages decreases as more are added because of the increase of D_{Al} with decreasing aluminum concentration in the solutions. The concentration of aluminum in the solutions of the wash stages decreases toward the extract exit end, and hence ϵ'_{Al} decreases in that direction. As the extract progresses through the wash stages then, a smaller fraction of the remaining aluminum in it is removed at each stage, and if ϵ'_{Al} decreases sufficiently, i.e., (becomes less than unity) the concentration of aluminum eventually reaches a value which is not further decreased.

TABLE XXXIII

The approximation of steady state concentrations in the two-solvent countercurrent extraction of an aqueous solution of thiocyanate, beryllium, and aluminum by conditioned MIK. (Calculations of Appendix 2)

No. of App.	Extract		Raffinate		Washed Extract		Feed	
	(Be^{+2})	(Al^{+3})	(Be^{+2})	(Al^{+3})	(Be^{+2})	(Al^{+3})	(Be^{+2})	(Al^{+3})
1	0.0333	0.0020	$(4)(10^{-4})$	0.0940	0.0222	$(4)(10^{-6})$	0.1333	0.1060
2	0.0443	0.0021	$(5.33)10^{-4}$	0.0996	0.0292	$(4.2)(10^{-6})$	0.1453	0.1063
3	0.0482	0.0021	$(5.81)(10^{-4})$	0.1000	0.0318	$(4.2)(10^{-6})$	0.1492	0.1063
4	0.0495	0.0021	$(5.97)(10^{-4})$	1.1000	0.0327	$(4.2)(10^{-6})$	0.1504	0.1063
5	0.0499	0.0021	$(6.02)(10^{-4})$	0.1000	0.0329	$(4.2)(10^{-6})$	0.1510	0.1063
6	0.0501	0.0021	$(6.04)(10^{-4})$	0.1000	0.0331	$(4.2)(10^{-6})$	0.1510	0.1063

APPENDIX 3

The Extent of Pairing of the Tetrahydrated Beryllium Ion with Halide or Pseudohalide Ions in Aqueous Solutions or Organic Solvents.

The extent of pairing of oppositely charged ions can be calculated from the radii and charges of the ions and the dielectric constant of the medium in which they exist by means of the Bjerrum Equation[36,37]:

$$K = \frac{4\pi N}{1000}\left(\frac{Z_1 Z_2 e^2}{k\,T}\right)^3 Q(b)$$

$$b = \frac{Z_1 Z_2 e^2}{a\,\epsilon\,kT}$$

where K = association constant of ion pairs

N = Avogadro's number

Z_1, Z_2 = charge on cation and anion

ϵ = dielectric constant of medium in which ions exist

e = charge on electron

T = absolute temperature

k = Boltzmann constant

a = distance of closest approach of ions of pair

= radius cation + radius anion

$Q(b)$ = a function of b which can be approximated by a method shown by Harned and Owen[37]

The radius of the tetrahydrated beryllium ion was obtained from the crystallographic data on beryllium sulphate tetrahydrate[84]. In the $Be(H_2O)_4^{+2}$ tetrahedron the distance between atomic centres are:

Be - O : 1.62 Å

O - O : 2.93 Å

On the assumption that the atoms are in contact this gives the radius of the $Be(H_2O)_4^{+2}$ ion as $1.62 + \frac{1}{2}(2.93) = 3.08$ Å.

The radii of the halide ions F^-, Cl^-, Br^-, and I^- were Pauling's values from tables of Durrant and Durrant[80]. The radius of the thiocyanate ion used was one half of the C ≡ N bond (also from Durrant and Durrant). This is justified by the fact that it is between these atoms that the electronic charge of the thiocyanate ion is in concentrated.

For pairs formed by the association of the $Be(H_2O)_4^{+2}$ ions with monovalent anions at 20°C the formulae reduce to:

$$K = \frac{(8.88)(10^7)Q(b)}{\epsilon^3} \quad \text{and}$$

$$b = \frac{(1.138)(10^{-5})}{a\epsilon}$$

Using these and the tables of Harned and Owen for Q(b) the following values of K shown in Table XXXIV were calculated.

These values indicate that pairing between the aquated beryllium ion and these anions is possible. Several factors would however make the actual association constants different from those indicated by this simple theory:

(1) In water, and to a lesser extent in organic solvents, the hydration spheres of the beryllium ion probably contain more than four water molecules,

(2) The larger anions would be considerably polarized by the beryllium ion, and

(3) Hydrogen bonding of the thiocyanate to the water molecules of the hydration spheres of the beryllium ion would increase the association of these ions.

The conclusions that can be drawn from these facts are:

(1) The association constants of the aquated beryllium ion and the chloride, fluoride and bromide ions in water are smaller than here indicated.

(2) The association constants of the aquated beryllium ion with thiocyanate and iodide ions in organic solvents are probably greater than here indicated, and

(3) The association constants of the aquated beryllium ion with iodide and thiocyanate ions in water may be either greater or smaller than here indicated, depending on the relative importance of factors (1), (2), and (3).

TABLE XXXIV

Extent of pairing of the tetrahydrated beryllium ion with monovalent anions in aqueous and organic media.

anion	radius anion (Å)	A (Å)	solvent	solv. 20°C (ɛ5)	b	Q(b)	K
F^-	1.4	4.5	H_2O	ɛ0	3.20	0.37	64
Cl^-	1.ɛ	4.9	H_2O	ɛ0	2.90	0.30	52
Br^-	2.0	5.1	H_2O	ɛ0	2.90	0.27	47
I^-	2.2	5.3	H_2O	ɛ0	2.6ɛ	0.24	42
SCN^-	0.6	3.7	H_2O	ɛ0	3.ɛ4	0.55	96.6
I^-	2.2	5.3	MlK	l3	16.4	$(2.14)10^2$	$(ɛ.6)10^6$
SCN^-	0.6	3.7	MlK	l3	23.6	$(3.9ɛ)10^4$	$(1.6l)10^9$
I^-	2.2	5.3	EtOEt	4.3	49.9	$(7.95)10^{14}$	$(ɛ.9)10^{20}$
SCN^-	0.6	3.7	EtOEt	4.3	71.5	$(3.9)10^{23}$	$(4.5)10^{29}$

BIBLIOGRAPHY

1. Burke, D. W., Jr. and White, J. E. The Metal Beryllium. American Society for Metals, Cleveland (1955).
2. Knoerr, A. W., Eng. Mining Jour., 93, September (1960).
3. (a) Chem. and Eng. News 42, 8, 27 (1964).
   (b) Ibid. 42, 9, 137 (1964).
4. Hessinger, P. S., Ind. Eng. Chem. 54, No. 3, 16.
5. Time, Can. Ed. 82, No. 19, 64 (1963).
6. Beaver, W. W. and Lumpany, B. B. Canadian Patent No. 668, 704. Selective Fluorination and Extraction of Beryllium Ores. Granted to the Brush Beryllium Company, Cleveland, Ohio, U.S.A., Aug. 13 (1963).
7. Moore, R. E., Shaffer, J. H., and McDuffie, H. J. The Preparation of High Purity Beryllium Oxide through the Acetylacetone - E.D.T.A. Solvent Extraction Process. ORNL - 3323. (1963).
8. Biermann, J. W., and Bennet, S. L., Can. J. Chem. 40, 73, (1962).
9. Biermann, J. W., and McCorkell, R., Can. J. Chem. 40, 1368 (1962).
10. Biermann, J. W. and McCorkell, R., Can. J. Chem. 41, 112 (1963).

12. Flagg, J. F., Chemical Processing of Reactor Fuels. Academic Press, New York (1961).

13. White, J. C. and Ross, W. J. Separations by Solvent Extraction with Tri-n-Octyl phosphine Oxide, Subcommittee on Radiochemistry, National Academy of Sciences - National Research Council. Washington, D.C. (1961).

14. Sandell, E. G., and Cummings, R. F., Anal. Chem. 21, 1356 (1949).

15. Solvent Extraction Chemistry Symposium. Nucl. Science and Eng. 16, No. 4, 381 (1963).

16. (a) Morrison, G. H., and Freiser, H., Anal. Chem. 34, 64R (1962).

(b) Ibid. 32, 37R (1960).

(c) Ibid. 30, 632 (1958).

(d) Craig, R. C., Anal. Chem. 28, 723 (1956).

(e) Ibid. 26, 110 (1954).

(f) Ibid. 24, 66 (1952).

(g) Ibid. 23, 41 (1951).

(h) Ibid. 22, 61 (1950).

(i) Ibid. 21, 85 (1949).

17. (a) Treybal, R. E., Ind. Eng. Chem. 54, No. 5, 55 (1962).

(b) Ibid. 53, No. 2, 161 (1961).

(c) Ibid. 52, No. 3, 262 (1960).

(d) Ibid. 51, No. 3, pt. II, 378 (1959).

(e) Ibid. 50, 463 (1958).

(f) Ibid. 49, 514 (1957).

(g) Ibid. 48, 510 (1956).

(h) Ibid. 47, 536 (1955).

(i) Ibid. 46, 91 (1954).

(j) Ibid. 45, 98 (1953).

(k) Ibid. 44, 53 (1952).

(l) Ibid. 43, 79 (1951).

(m) Elgin, J. C., Ind. Eng. Chem. 42, 47 (1950).

(n) Ibid. 41, 35 (1949).

(o) Ibid. 40, 50 (1948).

(p) Ibid. 39, 25 (1947).

18. Irving, H., and Williams, R. J. P., J. Chem. Soc. 1841 (1949).

19. Morrison, G. H., and Freiser, H., Solvent Extraction in Analytical Chemistry. John Wiley and Sons, Inc., New York (1957).

20. Nachtrieb, N. H., and Conway, J. G., J. Am. Chem. Soc. 70, 3547 (1948).

21. Sato, J., J. Inorg. Nucl. Chem. 26, 311 (1964).

22. Davies, M. and Gwynne, E., J. Am. Chem. Soc. 74, 2748,(1952).

23. Diamond, R. M., and Tuck, D. G., Extraction of Inorganic Compounds into Organic Solvents. In Progress in Inorganic Chemistry, Vol. II. Edited by F. A. Cotton. Interscience Publishers, New York (1960).

24. Irving, H., Rossotti, F. J.C., and Williams, R. J. P., J. Chem. Soc. 1906 (1955).

25. Moore, T. E., Gootman, R. W., Slezak, B. S. and Yates, P. C., J. Phys. Chem. 60, 504 (1956).

26. Laurence, A. H., Campbell, D. E., Wiberly, S. E. and Clark, H. M., J. Phys. Chem. 60, 901 (1956).

27. Saldeck, J., J. Phys. Chem. 60, 500 (1956).

28. Irving, H. M., Quart. Rev. 5, 200 (1951).

29. Diamond, R. M., J. Phys. Chem. 67, 2513 (1963).

30. Kolthoff, J. M. and Sandell, E. B., J. Am. Chem. Soc. 63, 1906 (1941).

31. Fierman, N. H., Mason, W. B. and Pekola, J. S., Anal. Chem. 21, 1356 (1949).

32. Huffman, E. H. and Beaufeit, J. J., J. Am. Chem. Soc. 71, 3179 (1949).

33. Sandell, E. B., and Cummings, P. F., Anal. Chem. 21, 1356 (1949).

34. Stary, J., and Hladky, E., Anal. Chem. Acta 28, 227 (1963).

35. Morris, D. F. C. and Bell, C. F., J. Inorg. Nucl. Chem. 10, 337 (1959).

36. Davies, C. W., Ion Association. Butterworth and Co., Toronto (1962).

37. Harned, H. S. and Owen, B. B., The Physical Chemistry of Electrolytic Solutions. Reinhold Publishing Corp., New York, (1950).

38. Alders, L., Liquid-Liquid Extraction. Elsevier, Amsterdam (1959).

39. Craig, L. C., Laboratory Extraction and Countercurrent Distributions. In Technique of Organic Chemistry. Vol. III, part I, second edition. Edited by A. Weisberger, Interscience Publishers, New York (1956).

40. Parry, R. W., and Keller, R. N. In The Chemistry of the Coördination Compounds. Edited by J. C.Bailar. Reinholt Publishing Corp., New York (1956),

41. Schwartzenbach, G., Bjerrum, J. and Sillen, L. Stability Constants, Part II: Inorganic Ligands. The Chemical Society, London (1958).

42. Ruzicka, J. and Stary, J., Substoichiometric Determination of Traces of Metals by Activation Analysis or by Isotope Dilution. Nuclear Energy Information Center, Czechoslovakia (1963).

43. Van Arkel, A. E., Molecules and Crystals in Inorganic Chemistry. Butterworth and Co., Toronto (1956).

44. Bock, R., Z. Anal. Chem. 133, 110 (1951).

45. Sundaram, A. K., and Banerji, S., Anal. Chem. Acta 8, 526 (1953).

46. Banerji, S., Sundaram, U. K. and Sharma, H. D., Anal. Chem. Acta 10, 256 (1954).

47. Merril, J. R., Honda, M. and Arnold, J. J. Anal. Chem., 32, 1420 (1960).

48. Buchanan, J. D., J. Inorg. Nucl. Chem. 7, 140 (1958).

49. Hardy, C. J., Greenfield, B. L. and Scargill, D. J. Chem. Soc. 174 (1961).

50. Tribalat, S., and Zeller, C., Bulletin de la Soc. Chem. de France, 2041 (1962).

51. Melnick, L., Freiser, H., and Beeghly, H. R., Anal. Chem. 25, 856 (1953).

52. Phipps, A. L., and Plane, R. A., J. Am. Chem. Soc. 79, 2458 (1957).

53. Moeller, J., and Zogg, R. E., Anal. Chem. 32, 612 (1950).

54. Tribalat, S., and Duthiel, C., Bull. Soc. Chem. de France, 196 (1960).

55. Garwin, L., and Hixson, A. N., Ind. Eng. Chem. 41, 2298 (1947).

56. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. J., Applied Inorganic Analysis. 2nd Edition. John Wiley and Sons, Inc., New York (1959).

57. Mellick, E. S., The Analytical Chemistry of Beryllium in Analytical Chemistry in Nuclear Reactor Technology. Edited by C. D. Susano, H. S. House, and M. A. Marler. AEC publication TIP-7555 (1958).

58. Welcher, F. J., The Analytical Uses of Ethylene-diaminetetraacetic acid. Van Nostrand, Princeton, N. J. (1958).

59. White, J. C., Meyer, A. S. and Manning, D. L., Anal. Chem. 28, 956 (1956).

60. Riley, J. M., A Rapid Method for Fluorometric Determination of Beryllium. U. S. Bureau of Mines, Report of Investigations 2582 (1956).

61. Wiberly, S. E. and Bassett, L. G., Anal. Chem. 21, 609 (1949).

62. Moeller, L., Ind. Eng. Chem., Anal. Ed. 15, 346 (1943).

63. Kolthoff, J. M., Elving, P. J., and Sandell, E. B., Treatise on Analytical Chemistry, Vol. 7, part II, page 89. Interscience Publishers, New York (1961).

64. Brubaker, C. H. and Johnson, C. E., J. Inorg. Nucl. Chem. 9, 184 (1959).

65. Katzin, L., J. Inorg. Nucl. Chem., 4, 187 (1957).

66. Alter, H. W., Codding, J. W. and Jennings, A. S., Anal. Chem. 26, 1357 (1954).

67. Irving, H. and Rossotti, F. H. C., J. Chem. Soc., 1927 (1955).

68. Goble, A. G., and Maddock, A. G., Trans. Far. Soc. 55, 591 (1956).

69. Templeton, C. C., and Daly, L. K., J. Am. Chem. Soc. 73, 3989 (1951).

70. Yates, P. C., Laran, R., Williams, R. E., and Moore, T. E., J. Am. Chem. Soc. 75, 2212 (1953).

71. Irving, H., and Rossotti, F. J. C., J. Chem. Soc. 1938 (1955).

72. Dyrssen, D., J. Inorg. Nucl. Chem. 8, 291 (1958).

73. Chatt, J., and Duncanson, L. A., Nature 178, 997 51-84, (1956).

74. Good, M. L., and Bryan, S. E., J. Am. Chem. Soc. 82, 5636 (1960).

75. Dwyer, F. P., and Gibson, N. A., Nature 168, 787 (1951).

76. Friedman, H. L., J. Am. Chem. Soc. 74, 5 (1952).

77. Taube, M., J. Inorg. Nuclear Chem. 12, 174 (1959).

78. Kolthoff, J. M., Belcher, R., Stenger, V. .A., and Matsuyama, G., Volumetric Analysis, Vol. III, page 419. Interscience Publishers, New York (1957).

79. Biermann, W. J., and Heinrichs, M., Can. J. Chem. 40, 1361 (1961).

80. Durrant, P. J., and Durrant, B., Introduction to Advanced Inorganic Chemistry. Logmans Green and Co., London (1962).

81. Gorman, M., and Connel, J., J. Am. Chem. Soc., 69, 2063 (1947).

82. Appleton, D. B., and Selwood, D. W., J. Am. Chem. Soc. 63, 2029 (1941).

83. Irving, H., and Rossotti, F. J. C., J. Chem. Soc. 1946 (1955).

84. Strukturbericht II, 91 (1928-1932), C. Herman, O. Lohrmann, and H. Philip. Edward Brothers Inc., Ann Arbor (1943).

85. Maryott, A. A., and Smith E. R., Table of Dielectric Constants of Pure Liauids. National Bureau of Standards Circular 514 (1951).