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# Sulfoxides as solvent extraction reagents for the analytical separation of metal ions

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**SULFOXIDES AS SOLVENT EXTRACTION REAGENTS**  
**FOR THE ANALYTICAL SEPARATION OF METAL IONS.**

**Iowa State University, Ph.D., 1969**  
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SULFOXIDES AS SOLVENT EXTRACTION REAGENTS FOR THE  
ANALYTICAL SEPARATION OF METAL IONS

by

David Colin Kennedy

A Dissertation Submitted to the  
Graduate Faculty in Partial Fulfillment of  
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Approved:

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1969

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## INTRODUCTION

In the search for new solvent extraction systems, the variable that can be most profitably exploited is the molecular configuration of the solvent extraction reagents themselves. Through the variation of molecular parameters such as type of functional group and molecular geometry, new and useful properties can be created. Thus, a vast amount of research has been devoted to the design, synthesis and evaluation of new organic compounds for use as solvent extraction reagents.

One particular class of reagents has received much attention in recent years. This class includes those unionized compounds (thus excluding liquid ion exchangers) which, through the action of a polar functional group, are able to solvate and extract metal-ligand complexes. Representative of compounds in this category are the well-known, neutral organophosphorous extractants, tri-n-butyl phosphate, tri-n-octyl phosphine oxide, and the bifunctional phosphine oxides such as methylene-bis(di-n-hexylphosphine oxide). All these compounds owe their solvent extraction properties to presence of the semi-polar phosphorous-oxygen moiety,  $\text{>P}\rightarrow\text{O}$ .

Another group of compounds, the sulfoxides, belong in the same category. These compounds contain the semi-polar sulfur-oxygen moiety  $\text{>S}\rightarrow\text{O}$ , which is very effective in solvating metal-ligand complexes. This ability is amply demonstrated by the simplest sulfoxide, dimethyl sulfoxide (DMSO), which forms a large number of metal complexes. Unfortunately, the higher molecular weight sulfoxides, unlike the analogous organo-phosphorous compounds, have received scant attention as solvent extraction reagents. The small amount of work that has been performed

has indicated that such sulfoxides are, indeed, excellent solvent extraction reagents.

On no occasion, however, has the solvent extraction behavior of sulfoxides been systematically and extensively studied. The purpose of the present study is: (1) to investigate and describe the interactions of a large number of metals with several representative sulfoxides in several acid-ligand systems, and (2) to evaluate these sulfoxides as analytical reagents by performing analytical separations.

It is hoped, that through this research, the full potential of sulfoxides as solvent extraction reagents will be clearly demonstrated and that this, in turn, will lead to the further study and use of sulfoxides in separation processes.



## THEORY AND BACKGROUND

Principles of Solvent Extraction and  
Reversed-Phase Partition Chromatography

Some general principles of solvent extraction and reversed-phase partition chromatography will now be discussed. It will not be the purpose of this discussion to render a detailed or rigorous treatment of the theory of solvent extraction and chromatography. Rather, only that information pertinent to the presentation of the results of the present research will be included. Those wishing more detailed information are referred to the works listed below.

A general treatment of solvent extraction is given by Berg (1), by Fomin (2), by Morrison and Freiser (3) and in the "Treatise on Analytical Chemistry" (4). Partition chromatography has been well covered in a book by Giddings (5) and the subject has been reviewed by Testa (6). Eschrich and Drent (7) have recently published a bibliography of reversed-phase chromatography complete with abstracts. Cerrai and Testa (8) have developed equations which relate extraction mechanisms to reversed-phase paper chromatography behavior. An excellent example of the application of reversed-phase paper chromatography to the evaluation of new solvent extraction reagents is presented by Cerrai (9).

Liquid-liquid solvent extraction

Liquid-liquid extraction is a partitioning process based on the selective distribution of a substance between two immiscible phases. A third component, when added to a two-phase system, will distribute itself between the two phases in a definite manner.

The extent of extraction of a particular species is usually described in terms of the distribution coefficient

$$K_D = \frac{M_2}{M_1} = \frac{\gamma_1}{\gamma_2} K'$$

where  $M_1$  and  $M_2$  refer to the molal concentrations of solute in the two phases,  $\gamma_1$  and  $\gamma_2$  to the activity coefficients, and  $K'$  is a constant provided the presence of the solute does not affect mutual solubility of the two phases (3).  $K_D$  remains constant then, provided the ratio of the activity coefficients remains constant.

The above considerations apply to the distribution of one species between two phases. Of more practical interest is the total amount of a substance extracted compared to the amount left in the other phase regardless of whether it is present in one or in several species in either phase. Knowledge of the stoichiometric ratio of the total concentration of a substance in one phase to its total concentration in the other phase is defined as the volume distribution ratio.

$$D_V = \frac{\text{Total concentration in organic phase}}{\text{Total concentration in aqueous phase}}$$

This is a generally more useful term than the distribution coefficient and will be the experimental parameter employed in the present work.

The distribution ratio can also be used to elucidate the nature of the extractable species. The following simplified equilibrium is often encountered in solvent extractions:



In equation 1,  $M^{+a}$  is a cation,  $Y^{-}$  is an anion, R is a solvent extraction reagent, and  $MY_a \cdot R_n$  is the extractable complex. If we assume that

$$D_V = \frac{[MY_a \cdot R_n]_{org.}}{[M^{+a}]_{aq.}}$$

and also assume activity coefficients are unity, the following relationship is established (10):

$$\log D_V = n \log [R]_{org.} + a \log [Y^{-}]_{aq.} + \log K_{eq.} \quad (2)$$

where  $K_{eq.}$  is the equilibrium constant of equation 1. Thus, a plot of log distribution ratio against log concentration of the extractant (dissolved in an inert diluent) at constant concentration of  $Y^{-}$  should give a straight line of slope "n". An analogous procedure is used to arrive at the value of "a".

Another term which is commonly used to express the degree of distribution is the percent of extraction, E, which is related to distribution ratio in the following way:

$$E = \frac{100 D_V}{D_V + V_a/V_o}$$

Generally,  $V_o$ , the volume of the organic phase and  $V_a$ , the volume of the aqueous phase are equal, thus, simplifying the relationship. When multiple extraction is employed with a fresh organic phase, the total percentage of solute extracted after n extractions ( $V_o = V_a$ ) is given by

$$\bar{E} = 100 - \frac{100}{(D_V + 1)^n} \quad (3)$$

The effectiveness of extraction techniques for two substances is usually described by means of a separation factor,  $\alpha$ .

$$\alpha = \frac{D_{V1}}{D_{V2}}$$

$D_{V1}$  and  $D_{V2}$  are the volume distribution ratios of the two extractable substances. It is apparent that two species will not be resolved with one extraction unless  $D_{V1}$  and  $D_{V2}$  are vastly different. In practice, the separation can only be accomplished if  $D_{V1}$  is greater than 100 and  $D_{V2}$  is less than 0.01 ( $\alpha = 10,000$ ). If one component is only partially extracted and the other is essentially not extracted, the mixture can still be separated by several consecutive extractions, the number necessary being determined by equation 3. If, however, both components are extracted, they cannot be resolved by repeated batch extraction, regardless of the magnitude of  $\alpha$ . Each extraction performed to remove another fraction of one component is always contaminated by the second.

Although countercurrent extraction techniques can be employed in such situations, for analytical separations this is generally impractical. Reversed-phase column chromatography has been shown to be the most satisfactory technique for accomplishing such separations.

#### Reversed-phase column chromatography

The technique of reversed-phase column chromatography involves the use of some inert, solid, supporting medium which is coated or impregnated with an extractant as a column packing material. The substances to be separated are placed on the column and eluted with an aqueous phase. Although absorption and other effects are possible, the various substances generally move down the column at rates inversely proportional to their

distribution ratios. One is able to calculate the retention volume,  $\bar{V}$ , the volume necessary to elute a substance to its maximum concentration.

$$\bar{V} = V_m + D_v V_s \quad (4)$$

The quantity  $V_s$  is the volume of the stationary phase and  $V_m$  is the volume of the mobile phase or interstitial volume. Thus, from a knowledge of the distribution ratios of two substances, a reversed-phase column can often be designed for their separation.

In practice, a limit is placed upon the magnitude of the distribution ratios and the separation factor. The distribution ratio of the metal being retained should be greater than 10 while that of the metal being eluted should be less than one. For a reversed-phase column of reasonable length, the separation factor should be greater than 10.

#### Reversed-phase paper chromatography

The technique of reversed-phase paper chromatography is directly related to the previously discussed technique of reversed-phase column chromatography. A sheet of filter paper serves as the inert, solid, supporting medium and is coated or impregnated with the extractant. The sheets are eluted with an aqueous solution by means of capillary action. Metals are partitioned between the mobile, aqueous phase and the immobile, extractant phase and move along the paper at rates inversely proportional to their distribution ratios.

Paper chromatography can be, and to some extent is, used as an analytical tool for separating mixtures of metals. However, its greatest utility lies as a qualitative technique for evaluating the interaction of metal ions with new extracting reagents. Using this technique, the

extraction of a large number of metals may be rapidly studied under a variety of conditions. Following this screening process, the more interesting systems may then be examined in greater detail using the more precise, but time-consuming, technique of solvent extraction. The two processes are similar enough to make paper chromatography data a valuable aid in predicting solvent extraction behavior.

The parameter most commonly measured in paper chromatography is  $R_f$ .

$$R_f = \frac{\text{Distance traveled by the metal}}{\text{Distance traveled by the eluent}}$$

Since the metal occupies a finite area, one point must be selected to define the distance traveled. Logically, the point of maximum metal concentration should be used but, since this is difficult to measure, the geometrical center of the metal spot is generally used as an approximation.

A more meaningful way of expressing paper chromatography data is to relate  $R_f$  to a distribution ratio. Cerrai and Testa (8) have derived the following equation:

$$D = \frac{A_m}{A_s} \left( \frac{1}{R_f} - 1 \right) = K \left( \frac{1}{R_f} - 1 \right)$$

The symbols  $A_m$  and  $A_s$  represent the cross sectional areas occupied by the mobile and stationary phases, respectively.

Just as for solvent extraction, paper chromatography distribution ratios can be used to deduce the nature of the extractable complex. Assuming the equilibrium described by equation 1 and using equation 2, one obtains;

$$\log(1/R_f - 1) = n \log[R]_{\text{paper}} + a \log[Y^-]_{\text{aq.}} + C \quad (5)$$

where  $C = \log K_{\text{eq.}} \cdot \frac{A_s}{A_m}$ .

The values of  $n$  and  $a$  are determined as previously described for solvent extraction except that the reagent concentration is now varied by impregnating the paper with varying amounts of reagent.

It should be noted that the paper chromatography ratio,  $D$ , is not the same as the volume distribution ratio,  $D_v$ , described previously for solvent extraction and column chromatography. Differences arise mainly from four sources.

- (1) Paper chromatography is a non-equilibrium process. Unlike column chromatography, the support is not equilibrated with eluent prior to sorption of metals. Consequently, at the solvent front, the eluent often undergoes partitioning which establishes acid concentration gradients.
- (2) The cellulose support is not entirely inert. Matrix effects may arise through the interaction of metals with the cellulose substrate. Cellulose, itself composed of polar carboxy groups, was used as an active partitioning medium for metals long before it was considered as an "inert" support for reversed-phase chromatography.
- (3)  $D_v$  and  $D$  are reagent concentration dependent. An exact agreement of  $D_v$  and  $D$  would be fortuitous as these values are a function of the reagent concentration in solution and on the paper, respectively. The problem is further complicated by the lack of a suitable means of expressing reagent concentrations

on paper.

- (4) The chemical environment of the reagent differs between paper and solution. Many solvent extraction reagents are solid materials and are so present on the paper, whereas for solvent extraction they are dissolved in a diluent. Furthermore, the choice of a diluent has a profound effect upon the solvent extraction behavior of many reagents. Diluents which interact strongly with the reagent, most commonly through hydrogen bonding, will depress the extraction of certain species. Non-polar diluents, on the other hand, may adversely effect some extractions owing to their inability to solvate ion association complexes. Even for the ideal case of a pure, undiluted, liquid extractant, the effect, although much smaller, may still prevent an exact correlation of  $D_V$  and  $D$  owing to an interaction between the cellulose and the extractant.

Despite these differences,  $D_V$  and  $D$  are usually quite similar in magnitude. Eluent partitioning, which effects only those metals with high  $R_f$  values, usually has a negligible effect upon the significance of the distribution ratios. Matrix effects, generally quite small for most metals in strong acids, can be easily recognized and compensated for by running "blank" chromatograms. The two distribution ratios can be made to agree even more closely by adjusting the experimental conditions. Non-equilibrium effects can be eliminated entirely by presoaking the chromatographic paper in the eluent and using descending elution techniques. Concentration effects can be compensated for by an adjustment of the reagent concentration on paper and in a diluent. Prudent



selection of the solvent extraction diluent is also indicated.

However, the extra effort and, more importantly, the extra time required to achieve a more exact correlation is not warranted for the purpose of evaluating new solvent extraction reagents. The two systems, solvent extraction and paper chromatography, need not correlate exactly-- they need merely exhibit analogous behavior. Hence, for the present research, the intrinsic similarity of  $D_V$  and  $D$  will be sufficient to make excellent use of the paper chromatography survey technique.

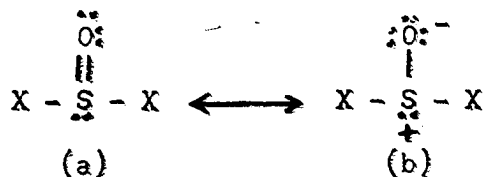
## Chemistry of Sulfoxides

### General considerations

The sulfoxides represent a family of sulfur compounds characterized by the formula  $R_2SO$ . The lowest member of the series, dimethyl sulfoxide (DMSO), is very well known and is noted for many unique chemical properties, including that of forming metal complexes. The higher members of the series, while not so familiar, retain many of the properties of dimethyl sulfoxide because they share a common functional group. Thus, an understanding of the nature of the sulfoxide group and of the complexing properties of dimethyl sulfoxide will be helpful in any discussion of sulfoxides as solvent extraction reagents.

The superficial structural resemblance of the sulfoxides to the ketones contrasts with the known differences in properties. The demonstration of optical isomerism in sulfoxides,  $R_1SOR_2$ , by the successful resolution of isomers (11) as well as studies of parachor (12) and bond refraction (13) are suggestive of marked differences between

sulfoxides and ketones. The sulfoxide bond is now thought to be a resonance hybrid of the following forms (14):



The question of resonance involving the d electrons of sulfur is not settled beyond all doubt. However, most workers believe (15) that structure (a) contributes very little and that the sulfur-oxygen linkage is best described as a semipolar, single bond represented as:



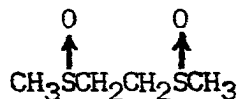
In view of this, sulfoxides still retain an unshared pair of d electrons; hence, the sulfoxide group does not have a strong attraction for electrons and does not undergo enolization (16).

Because of the possibility of nucleophilic attack on the sulfur atom, sulfoxides are subject to a number of reactions such as oxidation to the sulfone, reduction to the sulfide, disproportionation, cleavage, and certain rearrangements (15, 17). This reactivity will prohibit the use of sulfoxides in certain solvent extraction processes; extractions from strong nitric acid, extraction of species such as cerium(IV), tin(II), etc. It has been reported (18) that chain branching increases the susceptibility of sulfoxides toward oxidation. Whereas bis(2-ethylhexyl)sulfoxide is unstable with respect to air oxidation and di-tert-butyl sulfoxide is very rapidly oxidized by air, di-n-octyl sulfoxide is completely stable.

The presence of the lone electron pair leads to a stable, pyramidal arrangement of groups around the sulfur atom (15). The R-S-O bond angles are remarkably constant ( $107^\circ \pm 1^\circ$ ) regardless of the nature of R (19). When the two groups attached to the sulfoxide moiety are different, the sulfur atom becomes a center of asymmetry and optical activity results. A number of optically active sulfoxides have been resolved. For example (20):



When two similar asymmetric sulfur atoms occur in the same molecule, meso and racemic mixtures should exist. This was well established by Bell and Bennett (21) for several compounds. For example:



meso form: melting point  $163^\circ - 164^\circ \text{ C.}$

dl form: melting point  $128^\circ - 130^\circ \text{ C.}$

The high polarity of the sulfoxide bond, average value of  $\mu_{\text{SO}} = 3.0\text{D}$  (22), leads to very strong participation in hydrogen bonding and dipole-dipole association (23, 24). The strong, electron donating properties of the oxygen atom enable the group to form complexes with Lewis acids (17). For example, the boron trifluoride complex of dimethyl sulfoxide,  $\text{BF}_3 \cdot \text{DMSO}$ , is quite stable and can be purified by sublimation (25). The oxygen terminal also accepts vacant orbitals of transition metals to form salts or complexes (26). There is a possibility that sulfoxides may also be able to coordinate with certain metals, such as palladium(II), by donating the lone pair of d electrons to a vacant metal orbital (26).

These interactions will now be discussed in greater detail in connection with the coordination chemistry of dimethyl sulfoxide.

#### Dimethyl sulfoxide-metal complexes

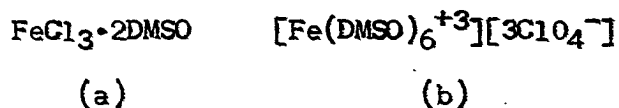
Dimethyl sulfoxide is a colorless, odorless, organic liquid which is highly polar, water miscible, and very hygroscopic. Of primary interest, for the purposes of this discussion, is the nature and extent of the solvating powers of dimethyl sulfoxide, especially with respect to inorganic salts. The ability of dimethyl sulfoxide to form complexes with metals will have relevance to the ability of higher molecular weight sulfoxides to extract these metals from aqueous solution.

Cotton and Francis (26), in a very exploratory and definitive work, observed the resemblance of the sulfoxides to the phosphine oxides which are known to form coordination compounds with Lewis acids and metal ions. They found sulfoxides to behave similarly and report the color and composition of many transition metal halide complexes with dimethyl sulfoxide. From their work it is evident that oxygen is the donor atom in nearly all cases. The exception is palladium(II) in  $\text{PdCl}_2 \cdot 2\text{DMSO}$  where infrared evidence suggests a  $\text{Pd} \leftarrow \text{S}$  coordination. These authors have predicted that similar bonds might occur in the complexes of platinum(II) and gold(III).

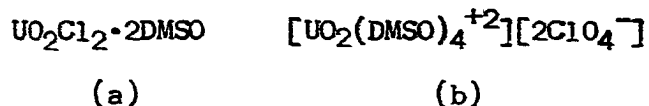
Meek and co-workers (27) studied the transition metal complexes of dimethyl sulfoxide and found them to have the general formula  $(\text{M}[\text{DMSO}]_n)(\text{MX}_4)$  where  $n$  is 4 or 6 and  $X$  is halogen. Using dimethyl sulfoxide as a solvent and cobalt(II) as a metallic ion they concluded

that chloride is more and iodide less-strongly coordinated than sulfoxide.

Selbin *et al.* (28) found that with divalent metals and iron(III), empirical formulas for metal-dimethyl sulfoxide complexes with halides generally show 1, 2 or 3 moles of dimethyl sulfoxide per mole of salt suggesting that an anion is coordinated. An exception is the aluminum (III) chloride complex which has 6 molecules of dimethyl sulfoxide in its structure. In perchlorate salts, complete solvation is generally attained. Thus, iron(III) forms two different species;



Likewise for uranium(VI) there are formed;



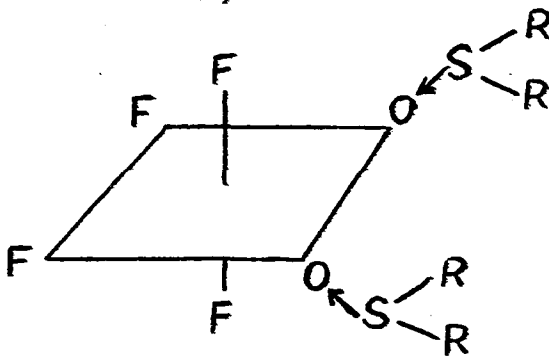
In their studies, they correlated the decrease in strength of the sulfur-oxygen bond in dimethyl sulfoxide with an increase in the strength of the metal-oxygen attraction and proposed the following stability series:

- (a) for divalent chlorides: Hg < Ni < Co < Cd < Pb < Cu
- (b) for divalent perchlorates: Ni < Mn < Co < Fe < Pb < Cu
- (c) for trivalent ions: Al < Ga < Fe

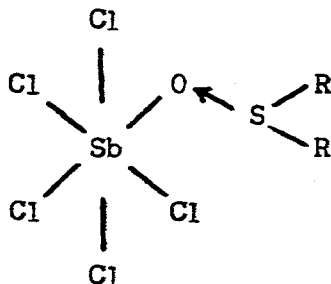
Gillette (29) studied the anion exchange behavior of a large number of metals in 0.6 molar hydrochloric acid-methanol-dimethyl sulfoxide. Anomalously low distribution ratios were obtained for certain metals (notably, molybdenum(VI), gold(III), uranium(VI), and iron(III)) at higher concentrations of dimethyl sulfoxide. This was attributed to the formation of strong, cationic, dimethyl sulfoxide complexes which inhibited the

formation of anionic or neutral chloride complexes which would be strongly absorbed by the resin.

The stereochemistry of some metal fluoride-dimethyl sulfoxide complexes was studied by Muettterties (30). He found that for  $TiF_4 \cdot 2DMSO$  and analogous compounds with silicon(IV), germanium(IV) tin(IV), and molybdenum(IV) the structure was;



In the case of the antimony(V) chloride complex,  $SbCl_5 \cdot DMSO$ , Lindquist and Einarsson (31) showed it to have the structure;



The bonding in most of the metal coordination complexes with dimethyl sulfoxide is quite strong, usually equivalent in strength to the corresponding aquo derivative (32). Hence, in the presence of an excess of water, most metal-dimethyl sulfoxide complexes are rapidly hydrolyzed. However, several of the metal-dimethyl complexes have been found to be unusually stable. The  $FeCl_3 \cdot 2DMSO$  complex has great thermal stability, the  $SnCl_4 \cdot 2DMSO$  complex can be prepared in aqueous solution

and may be sublimed at 180° C. without decomposition (26), and the  $\text{TiF}_4 \cdot 2\text{DMSO}$  complex can be recrystallized from water (30).

### Sulfoxides as Potential Solvent Extraction Reagents

The principles of solvent extraction and the chemistry of sulfoxides have previously been discussed. The chemistry of solvent extraction processes will now be examined. The purpose of this section will be to determine the position of sulfoxides in the spectrum of solvent extraction reagents and to anticipate some general results of the study of their solvent extraction properties.

#### Classification of solvent extraction reagents

Morrison and Freiser (3) have divided solvent extraction reagents into two main categories: chelating extractants and ion association extractants. The ion association extractants are further divided into the following three groups of reagents:

1. Liquid ion exchangers. Water immiscible amines, carboxylic acids, sulfonic acids, phosphoric acids, etc. which operate, at least formally, through the exchange of ionic species to form ion association complexes.
2. Solvating reagents. Compounds such as ethers, alcohols, and ketones, which contain a polar functional group capable of solvating and extracting metal-ligand complexes.
3. Coordinating reagents. Compounds such as phosphate esters, phosphine oxides, and amine oxides which contain a very polar functional group capable of forming extractable coordination complexes with metals

and metal complexes.

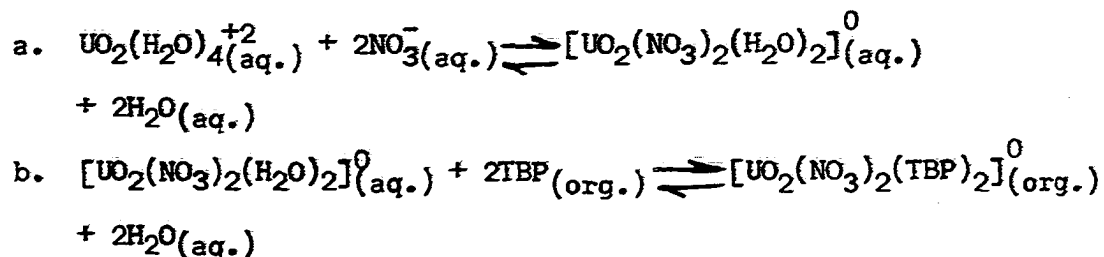
Categories 2 and 3 are fundamentally the same and differ only in the relative reagent-ligand strengths. For the purposes of this discussion, both groups will be included in the same category and will be referred to as neutral polar extractants.

### Some phosphoryl extractants

Two typical and well-known examples of neutral polar extractants are tri-n-butyl phosphate (TBP) and tri-n-octyl phosphine oxide (TOPO). Both compounds owe their strong coordinating ability to the presence of the phosphoryl moiety,  $\text{>P}\rightarrow\text{O}$ . The phosphorus-oxygen linkage, like the sulfur-oxygen linkage of sulfoxides, is best classified as a semipolar single bond with very little double bond character (33). In TBP, the presence of the butoxy groups reduces the polarity of the phosphoryl group relative to TOPO. Consequently, TBP is a weaker donor and a generally weaker extractant than TOPO (9).

Both compounds operate through two mechanisms of extraction, each involving the displacement of water molecules and the formation of a neutral complex. Both mechanisms will be illustrated for the case of uranium(VI) and TBP (34).

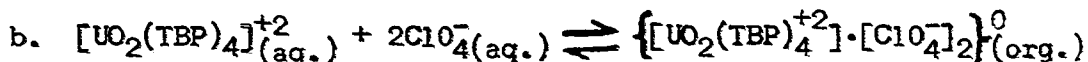
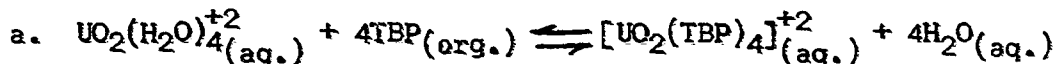
#### 1. Solvation of a neutral, metal-ligand complex





This mechanism predominates when neutral, metal-ligand complexes can readily be formed in aqueous solution. Thus, extraction is to some extent predictable from a knowledge of the equilibrium distribution of metal-ion complexes.

2. Ion pair formation



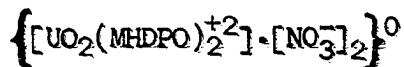
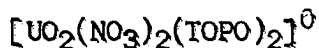
This mechanism is favored in the presence of an anion, such as perchlorate, which has weak coordinating powers of its own. The perchlorate ion also has spherical charge distribution which promotes the solvation of the ion pair in the organic phase. Mechanism 2 is observed in the presence of anions other than perchlorate when the neutral donor molecule is a stronger ligand than the anion for the particular metal being extracted (35).

Both mechanisms require the displacement of coordinated water molecules to give an extractable species. Owing to steric hindrance, it is difficult to place large numbers of bulky, organic ligands around a metal ion. Thus, mechanism 2 is not favored for metals of high coordination number and even for uranium(VI) the extraction is not extremely high (34). In such cases, mechanism 1 is favored because the displacement of water molecules is assisted by the counter anion. In some instances, however, even this is not sufficient to give extraction. The lanthanides form strong nitrate complexes (36), but their high coordination numbers make it difficult to displace the necessary waters of hydration with a simple ligand like TBP. Hence, the extraction by

mechanism 1 is relatively weak and mechanism 2 is not observed to any extent at all.

Bifunctional phosphine oxides, such as methylenebis(di-n-hexylphosphine oxide) (MHDPO) represent a significant advance over the monofunctional phosphine oxides (35). MHDPO is able to function as a bidentate ligand through the formation of a chelate ring, resulting in a much stronger complex than is possible with monodentate ligands. Apparently, only the first two members of the series of bis phosphine oxides are able to coordinate in this manner. When the functional groups are separated by more than two carbon atoms, chelating ability is lost and these materials extract much as monofunctional phosphine oxides. Bidentate coordination is also significant in that it requires a fewer number of ligands to achieve the same degree of coordination, which reduces steric hindrance effects. Thus, when the extraction is by mechanism 2, the bis phosphine oxides show a spectacular improvement over monofunctional phosphine oxides. The distribution ratios for the extraction of uranium(VI) from perchloric acid with MHDPO are three to five orders of magnitude greater than those for TOPO (37). MHDPO also strongly extracts the lanthanides from perchloric acid (38-40), a clear manifestation of mechanism 2.

When extraction by mechanism 1 is expected, MHDPO also is superior to TOPO, although not so dramatically as previously described. In many cases where TOPO extracts by mechanism 1, MHDPO now extracts by mechanism 2. For example, in the extraction of uranium(VI) from nitric acid the following species are formed (35):



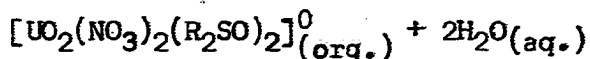
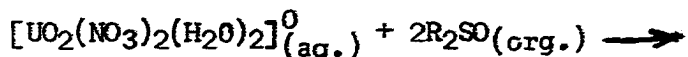
MHDPO is such a strong ligand that it is able to compete favorably with ions such as chloride and nitrate for positions in the inner coordination sphere of certain metals.

### Results expected for sulfoxides

The justification for anticipating that water insoluble sulfoxides should possess excellent solvent extraction properties is now apparent. The striking analogy between the sulfoxide and the phosphine oxides has been demonstrated. The validity of this comparison is reinforced by the existence of numerous metal complexes of dimethyl sulfoxide. From these observations, certain general predictions can be made concerning the results to be expected from a study of the solvent extraction properties of sulfoxides. (The small amount of work reported in the literature will be discussed in a later section.)

For monofunctional sulfoxides, three mechanisms of extraction can be expected.

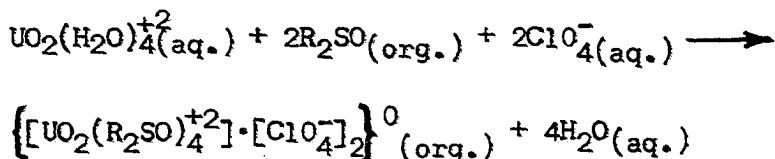
1. Solvation of a neutral, metal-ion complex by the sulfinyl oxygen



By this mechanism, we will expect to see the extraction of iron(III), gallium(III), antimony(V), tin(IV), molybdenum(VI), gold(III), uranium(VI), etc. from aqueous chloride solutions;

thorium(IV), uranium(VI), zirconium(IV), bismuth(III), etc. from aqueous nitrate solutions, and thorium(IV), uranium(VI), titanium(IV), zinc(II), etc. from aqueous thiocyanate solutions.

2. Solvation of a cation by the sulfinyl oxygen followed by ion pair formation.



Because of the difficulty in solvating cations with high coordination numbers, only the extraction of uranium(VI) from aqueous perchlorate will be expected by this mechanism. The uranyl ion is favored by its low coordination number (four) and by its sterically unhindered, square planar geometry.

3. Mechanism 1 or 2 accomplished by solvation through the sulfinyl sulfur atom.

Based on the existence of the analogous DMSO complex, we will expect strong extraction of palladium(II) (and possibly gold(III)) from aqueous chloride solution through solvation of a neutral chloro-complex. In view of the low coordination number of palladium(II), we might also expect extraction from perchlorate media by ion pair association.

We will expect especially strong extraction for a number of metals owing to the unusually high stability of their DMSO complexes. They are: Molybdenum(VI), tin(IV), titanium(IV), antimony(V), iron(III), gold(III), and uranium(VI).

For bifunctional sulfoxides, where the sulfinyl groups are separated by one and two carbon atoms, we will expect to observe bidentate coordination through chelate ring formation. This should manifest itself in the strong extraction of the lanthanides from nitrate solutions and in exceptionally strong extraction of uranium(VI) from perchlorate solutions.

A prediction of the extractive power of the sulfoxides relative to phosphoryl extractants is more difficult to make. This will largely be determined by the interaction of three factors.

1. The polarity of the  $\text{>S}\rightarrow\text{O}$  group compared to the  $\text{>P}\rightarrow\text{O}$  group.
2. The relative amount of steric hindrance.
3. The comparative degree of basicity which will determine the extent of competitive extraction of mineral acids.

The relative polarities of sulfinyl and phosphoryl compounds can be estimated by comparing their dipole moments. Table 1 lists the experimentally measured dipole moments of some polar compounds (41).

Table 1. Dipole moments of some polar compounds in benzene at 25°C.

Compound	Dipole moment (Debye units)
$(\text{C}_6\text{H}_5)_3\text{As}\rightarrow\text{O}$	5.54
$(\text{C}_6\text{H}_5)_3\text{P}\rightarrow\text{O}$	4.34
$(\text{C}_6\text{H}_5)_2\text{S}\rightarrow\text{O}$	4.00
$(\text{C}_6\text{H}_5\text{O})_3\text{P}\rightarrow\text{O}$	2.84
$(\text{CH}_3)_3\text{N}\rightarrow\text{O}$	5.03
$(\text{CH}_3)_2\text{S}\rightarrow\text{O}$	3.90
$(\text{CH}_3\text{O})_3\text{P}\rightarrow\text{O}$	3.02

Table 1 (Continued)

Compound	Dipole moment (Debye units)
$(\text{CH}_3)_2\text{C}=\text{O}$	2.89
$(\text{C}_2\text{H}_5)_2\text{O}$	1.15
$(i\text{-C}_4\text{H}_9)_2\text{S}\rightarrow\text{O}$	3.93
$(n\text{-C}_4\text{H}_9\text{O})_3\text{P}\rightarrow\text{O}$	3.05

From Table 1, it appears that sulfoxides should possess stronger solvating powers than the corresponding phosphate esters. Based on the limited comparison of the dipole moments of their phenyl derivatives, sulfoxides may approach the phosphine oxides in solvating power. Unfortunately, no comparative data could be found for alkyl phosphine oxides.

The ability to extract mineral acids, a function of basicity, is also related to bond polarity and will probably fall in the same order-- phosphates < sulfoxides < phosphine oxides. This is a very important consideration as it places a limit on the polarity of the molecules used as extractants. The amine oxides and arsine oxides are very polar compounds (Table 1) and should be excellent donors and extractants for metals and metal complexes. However, this is not observed in most cases because their great basicity results, instead, in the extraction of mineral acids (42). Likewise, TBP, although a poorer donor, is a better extractant than TOPO in very strong mineral acids; for example, in the extraction of the lanthanides from concentrated nitric acid.

The relative degree of steric hindrance is not easily arrived at. It would seem that sulfoxides should be much less hindered because they possess but two substituents whereas phosphates and phosphine oxides possess three. However, sulfoxides also have a lone electron pair which, although not as bulky as an alkyl group, adds to the steric hindrance. As a result, sulfoxides should be less hindered than the corresponding phosphoryl compounds, but not greatly so. The effect on extraction will probably not be noticeable except in situations where ligand-metal ratios are high.

In conclusion, sulfoxides should be superior to TBP in their extractive ability as a result of stronger ligand properties and smaller interference from steric hindrance. This order may be reversed in strong acid owing to stronger competitive extraction by the sulfoxides. Likewise, sulfoxides should be generally weaker extractants than phosphine oxides but may be comparable in situations which involve extraction from strong acids and extraction of complexes with high extractant-metal ratios. For certain metals, notably palladium(II) and gold(III), the extraction by sulfoxides should be superior owing to the unique possibility of strong sulfur-metal bonding.

#### Survey of the Literature

As we have seen, sulfoxides show every promise of being excellent solvent extraction reagents. However, there has been very little reported information concerning these compounds. A search of the literature has revealed only 11 references to the use of sulfoxides in solvent extraction processes. Of these, only five references are of sufficient depth

and substance to be considered as significant contributions to the understanding of the problem. This is in contrast to the case of the analogous, neutral, organo-phosphorous compounds. A recent review (43) lists over 100 papers (published in, roughly, a two-year period) which deal with these materials. Clearly, sulfoxides, by comparison, are ill-characterized. Little is known about their properties, behavior, or extent of application.

The earliest reference to the use of a sulfoxide as an extractant is in the work of Herrin (44) who studied the extraction of uranium(VI) from nitrate solutions using di-n-octyl sulfoxide dissolved in cyclohexane. The effects of changes in the concentration of nitrate ion, hydrogen ion, and di-n-octyl sulfoxide were investigated. The author concluded from his study that the extractable species had the composition  $UO_2(NO_3)_2 \cdot (R_2SO)_2$ .

Korpak studied the extraction of mineral acids and uranium salts and reported his findings in three parts. In Part I (45) he discussed some theoretical problems concerning the partitioning of mineral acids and uranyl salts between water and organic extractants. It was predicted that alkyl sulfoxides ought to be analogous to the alkyl phosphates and phosphine oxides in their extractive power.

The extraction of mineral acids by some alkyl sulfoxides was investigated in Part II (46). The order of extraction of the acids was found to be  $HNO_3 > HClO_4 \gg HCl$ . The compositions of the extractable species were reported as  $R_2SO \cdot HNO_3$ ,  $R_2SO \cdot HClO_4$ , and  $R_2SO \cdot HCl$ .

In Part III (47), Korpak investigated the extraction of uranyl



nitrate and chloride by di-n-octyl sulfoxide dissolved in carbon tetrachloride. The extractable complexes were found to be:  $UO_2(NO_3)_2 \cdot (R_2SO)_2$  and  $UO_2Cl_2 \cdot (R_2SO)_2$ . From the infrared spectrum of the latter complex, the author concluded that the uranium is bonded through the oxygen of the sulfoxide and not through the sulfur.

Guar and Mohanty (48) reported the extraction of thorium(IV) from hydrochloric acid by di-n-pentyl sulfoxide dissolved in carbon tetrachloride. The extraction was observed to go through a maximum at 8 M hydrochloric acid. The authors did not report the composition of the extractable complex, but their data indicate that the combining ratio of di-n-pentyl sulfoxide to thorium(IV) is 3:1.

In a later paper (49), the same authors reported the extraction of thorium(IV) from hydrochloric acid by mixtures of di-n-pentyl sulfoxide and tri-n-butyl phosphate. A synergetic effect upon the extraction was noted for these mixtures.

Webb (50) found di-n-octyl sulfoxide in a non-polar solvent to be a satisfactory reagent for the extraction and determination of gold(III). The complex, extracted from one to nine molar hydrochloric acid, was found to absorb strongly at 334 m $\mu$ . Iron(III) was also found to be strongly extracted and constituted an interference in the determination of gold unless fluoride was present. The extraction and interference of a number of other metals was also studied.

A report from Oak Ridge National Laboratory (51) briefly describes some exploratory work with a series of symmetrical alkyl sulfoxides. Surprisingly, they report that few metal ions were extracted from

chloride and nitrate solution and conclude that coordination takes place exclusively through the sulfur atom, rather than the oxygen atom of the sulfoxide.

In a subsequent report (52) this conclusion was again put forth after the study of a series of seven symmetrical alkyl sulfoxides. From the work of this author and others, however, it appears that this conclusion is erroneous and that the reagents under investigation may not have been properly evaluated. Contamination of the sulfoxide by the corresponding sulfide is a likely possibility.

Mohanty and Nalini (53) reported the extraction of zirconium(IV) from hydrochloric acid by di-n-pentyl sulfoxide in carbon tetrachloride. They concluded that this sulfoxide is as effective as tri-n-butyl phosphate for the extraction of zirconium.

Most recently, Torgov et al. (54) studied the extraction of uranium(VI) from nitrate solutions by di-n-octyl sulfoxide in benzene and carbon tetrachloride. They compared the extractions by sulfoxides to those by trialkyl phosphates and amine oxides.

## EXPERIMENTAL

## Apparatus

Paper chromatography: Pyrex jars, 12 inches high and 16 inches o.d. with circular plate glass covers were used for chromatographic tanks. Rectangular frames 23 cm. wide and 28 cm. high, constructed of 6 mm. glass rod, were used to support chromatographic paper of the same dimensions. At the top of each frame were 2.5 cm. horizontal extensions which allowed the frames to be vertically suspended in the tanks from a glass rod framework. The framework, a cube of 7 mm. glass rod measuring 29 cm. on a side, could accommodate eight of the paper-supporting frames.

Solvent extraction: Extractions were generally performed in 125 ml. Kimax separatory funnels with ground glass stoppers and one-way Teflon stopcocks. For some studies, extractions were performed in 16 x 150 mm. Pyrex culture tubes with screw-on plastic caps.

Column chromatography: Columns of several different dimensions, constructed of Pyrex tubing, were used. The liquid flow through the column was controlled with a one-way Teflon stopcock in the middle of a 7 cm. Pyrex tube with a 1 mm. bore. The chromatographic support was held in the column by a glass wool plug in the bottom. To prevent disruption of the support while adding eluents, a nylon fabric disc, held in place by a perforated Teflon disc, was situated on top of the bed. When hydrostatic pressure was not sufficient to give a reasonable flow rate of eluent through the column, air pressure, controlled by a Johnson regulator, was employed. A WCLID 1205 Series Automatic Fraction Collector, manufactured by Warner-Chilcott Laboratories Instruments Division, was used in conjunction with the chromatographic columns. Column effluents

were dispensed from a 3 ml. volumetric siphon.

Radiochemical equipment: A Nuclear Chicago Anti-Walk Single Channel Analyzer Model 27352 spectrometer was used to isolate gamma emissions from the tracers used. A Nuclear Chicago Decade Scaler Model 27104 counted the pulses received from the spectrometer. The detector used was a 3 x 3 inch NaI(Tl) scintillation crystal from the Harshaw Chemical Company. Thermal neutron irradiations were performed at the Ames Laboratory Research Reactor. Gamma spectra were recorded and analyzed with the Ames Laboratory's 1600 channel analyzer and associated computer facilities.

Spectrophotometer: A Cary Model 16 spectrophotometer was used for the spectrophotometric determination of trace amounts of uranium(VI) as the Arsenazo I complex. Five centimeter matched pyrex cuvettes were used as sample containers.

Apparatus used to characterize organic compounds: Infrared spectra were obtained with a Perkin Elmer Model 21 Double Beam Infrared Spectrophotometer using 0.2 mm. sodium chloride cells. A Cary Model 14 Recording Spectrophotometer was used to obtain ultraviolet spectra. One centimeter matched silica cuvettes were used as sample holders. The mass spectra of compounds were obtained with an Atlas MAT CH4 mass spectrometer. A Varian Associates A-60 Nuclear Magnetic Resonance Spectrometer was used to obtain proton spectra.

#### Reagents

Sulfoxides: Di-n-butyl sulfoxide (DBSO) and p-tolyl sulfoxide (PTSO) were obtained from the Aldrich Chemical Company. Bis(2-ethylhexyl)

sulfoxide (BEHSO) was obtained from the Columbia Organic Chemical Company. Di-n-octyl sulfoxide (DOSO), bis(n-octylsulfinyl)methane (BOSM), and bis(n-octylsulfinyl)ethane (BOSE) were synthesized as described in RESULTS AND DISCUSSION.

Metal salts: All metals used for this investigation, except as noted below, were obtained from normal commercial sources as the reagent grade metal, salt, or oxide. Uranyl perchlorate tetrahydrate was prepared from uranium dioxide which was obtained from the Ames Laboratory of the U. S. Atomic Energy Commission. The oxide was dissolved in hot, concentrated perchloric acid to give, after volume reduction and cooling, a quantity of hydrated salt. This material was then purified by twice recrystallizing it from water.

Anhydrous thorium tetrachloride was obtained from the Ames Laboratory. The material had been prepared by the reaction of the oxide with phosgene and was purified by triple vacuum distillation.

Zirconyl chloride octahydrate and hafnyl chloride octahydrate were obtained from the Ames Laboratory and purified by recrystallizing several times from 6 M hydrochloric acid. Emission spectrographic analysis showed the zirconium salt to contain less than 200 parts per million hafnium and the hafnium salt, less than 100 parts per million zirconium.

The series of lanthanide nitrate solutions used in paper chromatography was prepared by dissolving the corresponding oxides, obtained from the Ames Laboratory, in nitric acid. The high-purity europium oxide (99.9+%) used in later quantitative work, had been purified by ion exchange at the Ames Laboratory.

Chromatographic supports: Whatman No. 1 Chromatography paper, in the form of 28.5 cm. x 32 cm. sheets, was used throughout the paper chromatography survey. The supports most extensively employed for column chromatography were 60-80 mesh XAD-2, a macroreticular, styrene-divinylbenzene copolymer obtained from the Rohm and Haas Company, and 60-80 mesh Tee-Six (Teflon) obtained from Analytical Engineering Labs, Inc. Microgranular Cellulose Powder, Whatman Chromedia CC31, was used in some work.

### Experimental Techniques

Paper chromatography: The sheets of chromatography paper were fastened to the glass frames with rubber cement except when strong nitric acid solutions were used as eluents. In such cases, owing to the deterioration of the cement, it was necessary to use Teflon clamps to hold the paper. The papers were impregnated with extracting reagent by dipping them in a 0.05 M solution of the sulfoxide in isopropyl alcohol (DOSO and PTSO) or 80% isopropyl alcohol - 20% chloroform (BOSM and BOSE).

The excess solution was allowed to drain off and the frames were suspended in a hood to permit all solvent to evaporate.

Metal ions were applied to the papers with wooden applicator sticks which had been dipped in solutions of the metal perchlorate (when possible), nitrate, or chloride. The solutions were of minimum concentration necessary to give a readily detectable spot, generally 0.01 M to 0.05 M. The metals were spotted one inch from the bottom of the papers at one inch intervals, thus, accommodating eight metals per paper.

This arrangement allowed a maximum of 64 chromatograms to be run in a single tank.

Two liters of eluent was added to each chromatographic tank and, after allowing an hour for equilibration, the frames were suspended in the tanks. When the eluent had risen to within one inch of the top of the papers, the frames were removed and the papers were dried. The papers were then sprayed with color-forming reagents (see Analytical Procedures) to determine the locations of the metal spots.  $R_f$  values were always calculated using the geometric centers of the metal spots, unless otherwise noted.

In certain cases, it was necessary to alter the impregnating procedure described above. The study of the interaction of the lanthanides in nitric acid with BOSE required that the papers be specially treated to prevent streaking of these metals. Before being impregnated with BOSE, the papers were precoated by dipping them in a solution of a polymer in an organic diluent, followed by air drying. In the same study, in an attempt to determine the combining ratio of BOSE with certain lanthanides, the amount of reagent put on the papers was varied by dipping the papers in solutions of BOSE of varying molarity. Finally, for most metal-eluent combinations, blanks were run. This simply required eliminating the impregnation step altogether.

**Solvent extraction:** To determine distribution ratios, equal volumes of pre-equilibrated extracting reagent and aqueous metal solution were pipetted into separatory funnels. The funnels were agitated until equilibrium was attained (usually, in less than five minutes) after which the phases were allowed to separate. Aliquots of the aqueous

phases were then taken for analysis. The volumes of each phase used in the extraction varied from 10-50 ml., depending upon the extent of extraction. When high distribution ratios were encountered, large volumes were employed so that a more accurate analysis could be made of the small concentration of metal remaining in the aqueous phase. When culture tubes were used for extraction vessels, the procedure was identical excepting that 5 ml. of each phase was always used and a 4 ml. aqueous aliquot was taken for analysis.

#### Column chromatography:

**Column packing:** A glass wool plug was placed in the bottom of the column and covered with the organic phase which consisted of a given concentration of sulfoxide in a diluent. The stopcock was opened until about one cm. of liquid remained in the column and the air had been displaced from the tip. Tee-Six powder was slurried with a known volume of organic phase ( $V_1$ ) and the mixture was poured rapidly into the column. The stopcock was immediately opened and the liquid was allowed to drain at a moderate rate into a graduated cylinder while, simultaneously, the column was being vibrated by beating it with a section of rubber vacuum hose. After the bed had settled, the column was tamped gently with a glass rod and discs of nylon cloth and perforated Teflon sheet were placed on top of the bed. The level of liquid was then allowed to fall to the top of the bed and the volume of organic phase collected ( $V_2$ ) was measured.

The column was filled with distilled water and eluted at maximum flow rate to displace the interstitial organic phase. The last 20 ml. of eluent were passed rapidly (about 10 ml. per minute) using air pressure



so as to prevent bleeding of the organic phase during future operations. The total volume of organic phase displaced during this stage was measured and is equal to  $V_m$ , the volume of the mobile phase. The volume of the stationary phase,  $V_s$ , could then be determined as;

$$V_s = V_1 - V_2 - V_m.$$

When XAD-2 was used as a solid support, a slightly different packing procedure was used. This material is less dense than the organic phases used, making it impossible to properly pack a slurry. Hence, the XAD-2 was first slurried with methanol and packed using the procedure previously described. The desired organic phase was then passed slowly through the column to the top of the bed, displacing the methanol. The effluent was collected and  $V_2$  was measured after adding water to the methanol solution. The interstitial volume was displaced with water and measured as before.

In an attempt to duplicate exactly paper chromatography behavior, a study was made of impregnated cellulose powder columns. Microgranular Cellulose Powder was slurried with a 0.05 M solution of DOSO in isopropyl alcohol. The slurry was suction filtered to remove excess solvent and air dried. The dry impregnated powder was back-washed with water to remove fine particles. The resulting aqueous slurry was then packed into a column using the techniques previously described.

**Column elution:** Prior to adding the sample, the column was equilibrated by eluting with the aqueous eluent. The sample was then added in the same concentration of acid as present in the eluent and quantitatively sorbed onto the column. Although an attempt was made to

keep the sample volume as small as possible (generally 2-5 ml.), the primary concern was to avoid a large concentration of metal which, through loading effects, would lower the distribution ratio. The column was then eluted at a rate of 1-3 ml. per minute using eluent which had been previously equilibrated with the organic phase. The effluent was collected at intervals and analyzed for its metal content.

Before attempting the separation of mixtures of metals, the elution behavior of individual metal ions was determined. The column effluent was collected at 3 ml. intervals with the automatic fraction collector and its metal content was determined colorimetrically or radiometrically. Alternatively, for a qualitative determination of the shape of the elution curve, spot tests were periodically made on the effluent. When metal mixtures were separated, these elution curves served as the basis for selecting fractions of effluent for analysis.

Special techniques: Special precautions had to be taken when the reversed-phase consisted of the sulfoxide in a volatile diluent such as chloroform. Even when using equilibrated solvents, the diluent was gradually removed from the top few centimeters of the column. The solid sulfoxide that remained caused irreversible sorption of certain metals, resulting in tailing and less-than-quantitative recovery of these metals. To prevent this, approximately 0.5 ml. of pure diluent was sorbed on the column to redissolve the solid sulfoxide, prior to adding the sample.

Once a Tee-Six or XAD-2 column was properly packed, it was unnecessary to dismantle it in order to prepare a new column containing a different stationary phase. The old stationary phase was simply washed off with methanol and a new one was added. In practice, various

sizes of columns were prepared in advance with methanol, and the desired stationary phases were added as needed.

### Analytical Procedures

Paper chromatography: Metals were detected by spraying with one of the following color-forming reagents:

1. a 50% solution of ammonium polysulfide in methanol
2. a 0.1% solution of Arsenazo I in 90% methanol-water.

Table 2 lists the metals studied and, according to number, their method of detection. For metals detectable by both reagents, the first number indicates the preferred method.

Table 2. Analytical methods used to detect metal ions on chromatography paper

Metal	Reagent	Metal	Reagent	Metal	Reagent
Be(II)	1	Cu(II)	2,1	In(III)	1
Mg(II)	1	Zn(II)	1	Sb(III),(V)	2
Al(III)	1	Ga(III)	1	Ba(II)	1
Ca(II)	1	As(III)	2	Hf(IV)	1
Sc(III)	1	Sr(II)	1	Pt(IV)	2
Ti(IV)	1	Y(III)	1	Au(III)	2
V(IV)	1	Zr(IV)	1	Hg(II)	2
Cr(VI)	1	Mo(VI)	2	Tl(I)	1
Mn(II)	2	Ru(III)	2	Pb(II)	2
Fe(III)	1,2	Pd(II)	2	Bi(III)	1,2
Co(II)	2,1	Ag(I)	2	La(III)→	
				Lu(III)	1
Ni(II)	2	Cd(II)	2	Th(IV)	1
				U(VI)	1,2

The group II metals and thallium(I) were often difficult to detect on chromatograms run in strong acid. Arsenic(III) was difficult to detect on chromatograms run in hydrochloric acid, probably due to volatilization of arsenic trichloride. Manganese(II) and zinc(II) were visible only immediately after spraying with reagent.

Solvent extraction and column chromatography:

Titration methods -

EDTA: Solutions of EDTA were standardized against standard zinc(II) using Naphthyl Azoxine S (NAS) indicator. Standard zinc(II) and copper(II) were prepared by weighing an appropriate amount of pure metal, dissolving it in nitric acid and diluting with water. Anhydrous thorium tetrachloride, dissolved in dilute hydrochloric acid and diluted with water, was also used as a standard titrant.

Thorium(IV) and bismuth(III): These metals were determined by direct titration at pH 2 using Xylenol Orange indicator.

Zirconium(IV), hafnium(IV), vanadium(IV), and indium(III): These metals were determined by back-titration with standard thorium(IV) at pH 2.0, after the addition of excess EDTA, using Xylenol Orange indicator. In the case of vanadium(IV), ascorbic acid was added and the titration was carried out at pH 2.5.

Copper(II), cobalt(II), and zinc(II): These metals were determined by direct titration with EDTA using NAS indicator according to the method of Fritz et al. (55). Pyridine was used as the buffer.

Cadmium(II), lead(II), nickel(II), aluminum(III), gallium(III), and titanium(IV): These metals were determined by back-titration with standard copper(II) at pH 5.5 - 6.0, after the addition of excess EDTA,

using NAS indicator. Pyridine was used as the buffer. In the case of titanium(IV), five drops of 30% hydrogen peroxide were added prior to the addition of the EDTA.

Manganese(II): Manganese(II) was determined by direct titration with EDTA at pH 8.5 using NAS as the indicator. Ascorbic acid was added to the samples prior to titration.

Tin(IV): Tin(IV) was analyzed (56) by boiling the samples for five minutes after the addition of 1 gm. of sodium chloride, 5 ml. of concentrated hydrochloric acid, 1 ml. of concentrated sulfuric acid, and an excess of EDTA. The solutions were cooled and the excess EDTA was back-titrated with standard copper(II) using NAS indicator and pyridine buffer.

Yttrium(III), scandium(III), cerium(III), cerium(IV), gadolinium(III), and lutecium(III): These metals were determined by direct titration with EDTA at pH 6.0 using Arsenazo I indicator according to the method of Fritz *et al.* (57). Pyridine was used as the buffer. In the case of cerium(IV), ascorbic acid was added prior to the titration.

Mercury(II): Mercury was determined (58) by direct titration with thioglycerol at pH 6 using Thiomichler's Ketone as an indicator. Pyridine was used as a buffer.

Antimony(III), antimony(V), and arsenic(III): These metals were determined by oxidation-reduction titration with potassium bromate according to the method of Vogel (59). Antimony(V) was first boiled with sulfurous acid to be reduced to antimony(III). Naphthol Blue-Black was used as an indicator.

**Chromium(III):** Chromium(III) was determined by oxidation-reduction titration with cerium(IV) according to the method of Vogel (59). The chromium(III) was first oxidized to chromium(VI) with ammonium persulfate-silver nitrate and then reduced with excess iron(II). Ferroin was used as an indicator.

**Uranium(VI):** Uranium(VI) was determined titrimetrically by the method of Sill and Peterson (60). The metal was reduced to uranium(IV) by passing through a lead reductor. An oxidation-reduction titration was performed using cerium(IV) titrant and ferroin indicator.

**Colorimetric methods -**

**Uranium(VI):** Uranium(VI) was determined colorimetrically at pH 7.5 as the Arsenazo I complex by the method of Fritz and Richard (61). A  $5 \times 10^{-4}$  M solution of Arsenazo I containing  $1 \times 10^{-5}$  M EDTA was used. The buffer used was a solution prepared by mixing equal volumes of 0.5 M triethanolamine and 0.25 M nitric acid. The uranium(VI) concentration range employed was  $0.02 - 4.0 \times 10^{-5}$  M.

**Palladium(II) and gold(III):** These metals were determined by measuring the absorption of their chloro-complexes at  $225 \text{ m}\mu$  in 0.1 N hydrochloric acid. Figure 1 reproduces the absorbance spectra of these two metals in 0.1 N hydrochloric acid. The molar extinction coefficients of Pd(II) and Au(III) at 225 m are  $1.61 \times 10^4$  and  $4.10 \times 10^4$ , respectively. The absorbances of the complexes follow Beer's law over the range studied;  $0.25 - 3.0 \times 10^{-5}$  M.

**Spot tests:** The elution behavior of metals on chromatographic columns was often qualitatively established by performing a colorimetric spot test on the effluent. Titanium(IV) was detected as the yellow,

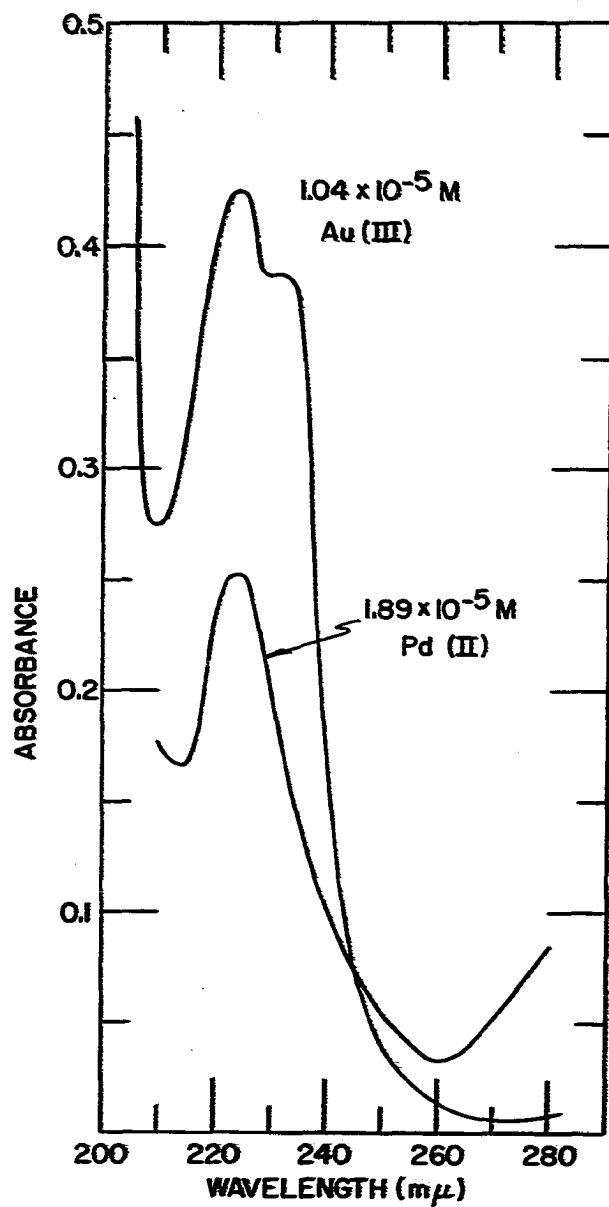


Figure 1. The ultraviolet absorption spectra of palladium(II) and gold(III) in 1 M hydrochloric acid

peroxy complex by adding a drop of 30% hydrogen peroxide to a drop of the column effluent. Thorium(IV) was detected as the Arsenazo I complex at pH 0-1. The stability of this complex in acidic solution makes it possible to detect thorium(IV) in the presence of most metals. Uranium (VI) was detected as the Arsenazo I complex at pH 6 using pyridine as a buffer. Zirconium(IV) and hafnium(IV) were also detected with Arsenazo I at pH 6. When using the automatic fraction collector, a slightly modified procedure was employed for these two metals. To the 3 ml. fractions of effluent in test tubes were added 2 ml. of  $5 \times 10^{-4}$  M Arsenazo I and 3 ml. of pyridine. The absorbances of the solutions were then measured at 590 m $\mu$ .

#### Radiometric methods -

Silver(I), cesium(I), barium(II), strontium(II), and iron(III): The distribution ratios of these metals were determined by measuring the distribution of the activity of a radioactive nuclide between the phases. The nuclides so employed were: Ag<sup>110-110m</sup>, Cs<sup>134</sup>, Ba<sup>133</sup>, Sr<sup>85</sup> and Fe<sup>59</sup>.

Hafnium(IV): The behavior of trace amounts of hafnium(IV) on reversed-phase columns was studied using Hf<sup>181</sup> tracer. Pure hafnium oxide was irradiated with thermal neutrons at the Ames Laboratory Research Reactor to an activity of 1 millicurie per mg. and dissolved in hydrochloric acid. The photopeak at 0.482 Mev. was counted.

Uranium(VI): Microgram amounts of uranium were determined by measuring the activity of fission products and Np<sup>239</sup> produced by the irradiation of a uranium(VI)-DOSO complex with thermal neutrons in the Ames Laboratory Research Reactor. Three standards, the sample, and a



blank were irradiated for two hours at a flux of  $3 \times 10^{13}$  neutrons per square centimeter per second. After allowing one day for decay of the initially very high activity, the gamma spectra were recorded using a 1600 channel analyzer. Computer treatment of the data yielded a graphical display of the energy and intensity of all photopeaks which lead to the easy identification of  $\text{Np}^{239}$  and various active fission products of  $\text{U}^{235}$ .

The activities of individual fission products in the sample, standards, and blank were then measured using a single channel analyzer. After subtracting the activity of the blank, the activity of each fission product was plotted against the amount of uranium present in the standards, yielding a series of calibration curves. From these curves, the activity of each fission product in the sample was related to an amount of uranium. The average of all these values was reported as the amount of uranium(VI) present in the sample.

## RESULTS AND DISCUSSION

## Synthesis, Purification and Characterization of Sulfoxides

Di-n-octyl sulfoxide (DOSO)

DOSO was prepared by oxidizing di-n-octyl sulfide with a slight excess of hydrogen peroxide using glacial acetic acid as a reaction medium. To avoid extensive over-oxidation, the reaction was run at room temperature and the hydrogen peroxide was added slowly as a dilute solution in glacial acetic acid. Following the two hour reaction period, a large amount of water was added and the solid sulfoxide was filtered off, washed with water, and air dried. This material was purified by crystallizing it twice from 95% ethanol. The melting point of the purified product, 71.5° - 72.5° C., corresponds well to the literature value (46). The infrared absorption spectra of DOSO in carbon tetrachloride is reproduced in Figure 2. The very broad, intense band centered at 1049  $\text{cm}^{-1}$  is typical of the absorption of aliphatic sulfoxides (24). The lack of peaks at  $1325 \pm 10 \text{ cm}^{-1}$  and  $1140 \pm 10 \text{ cm}^{-1}$  indicates that di-n-octyl sulfone, the over-oxidation product, is absent. The peak at 3450  $\text{cm}^{-1}$  is due to the O-H stretch of water molecules associated with the sulfoxide group and is typical of hydrated, polar extractants.

The purification of DOSO by crystallization is an important step as it insures the absence of any unoxidized di-n-octyl sulfide. This material can be expected to have coordinating properties of its own toward such metals as palladium(II) and gold(III). Thus, its presence would compromise any observation of sulfur-metal interaction for

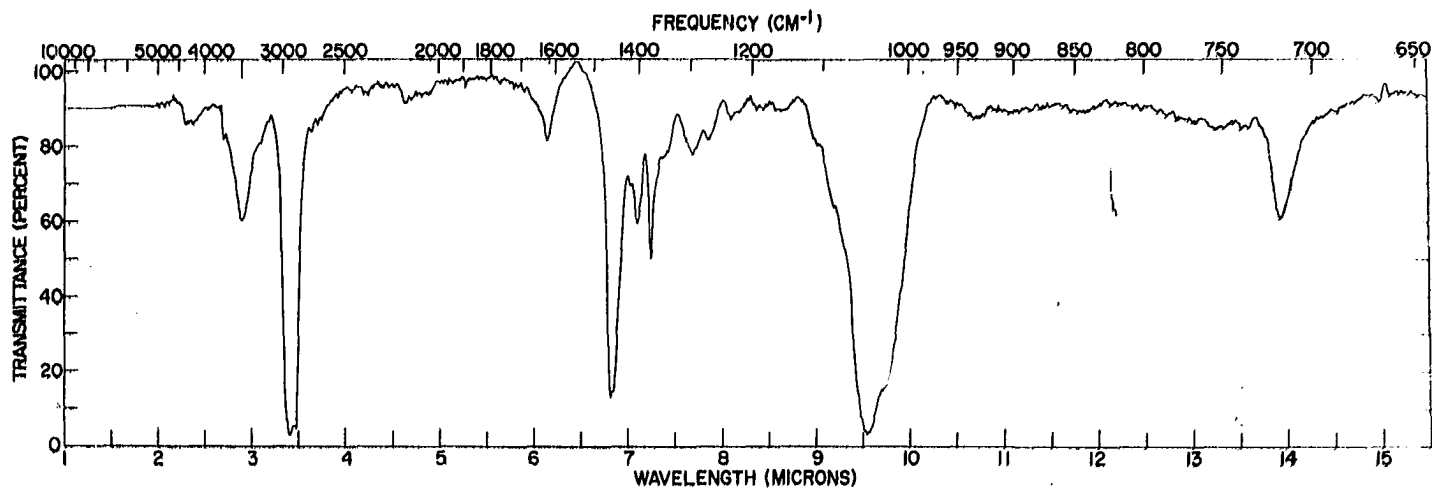


Figure 2. The infrared absorption spectrum of di-n-octyl sulfoxide in carbon tetrachloride

sulfoxides. The presence of a di-n-octyl sulfone impurity would not be so serious. This compound (and sulfones in general) can be expected to be nearly inert toward forming extractable coordination complexes with metals (62). This was confirmed experimentally and will be discussed in a later section.

bis(n-Octylsulfinyl)methane (BOSM)

The corresponding sulfide was first prepared by refluxing n-octyl mercaptan for two hours with an excess of di-iodomethane in the presence of ethanolic potassium hydroxide. The product was purified by extracting several times with an aqueous ethanol solution followed by several extractions with water. After drying over anhydrous sodium sulfate, the sulfide, in glacial acetic acid, was oxidized with hydrogen peroxide. To avoid over-oxidation, a slight excess of a dilute solution of hydrogen peroxide in glacial acetic acid was added slowly and the mixture was allowed to react at room temperature overnight. A large amount of water was added to precipitate the sulfoxide which was then filtered, washed with water, and air dried. The crude BOSM was recrystallized several times from 95% ethanol until the sulfone peaks in the infrared spectra of the compound were reduced to a low, constant level.

The final product, a soft, waxy solid, melted in the range 112 - 114°C. The mass spectra revealed a prominent peak at  $m/e$  336 which corresponds to the molecular weight of the parent ion of the bis sulfoxide. A peak at  $m/e$  338, 10% of the intensity of the  $m/e$  336 peak, is indicative of the presence of two sulfur atoms in the parent ion. A peak was observed at  $m/e$  352 with 4% of the intensity of the parent ion. This

ion, which also appears to contain two sulfur atoms, corresponds to a species containing one sulfoxide group and one sulfone group. A peak was also observed at  $m/e$  378 with an intensity of less than 1% of that of the parent ion. The position of this peak corresponds to the molecular weight of the bis sulfone.

The infrared spectra of BOSM in chloroform (Figure 3) shows a very intense, broad band centered at  $1033 \text{ cm.}^{-1}$  indicative of the sulfoxide group. The shift to lower frequency (compared to DOSO) is due to hydrogen bonding with the chloroform solvent. The existence of a small amount of sulfone impurity is indicated by the two weak peaks at  $1136 \text{ cm.}^{-1}$  and  $1321 \text{ cm.}^{-1}$ .

The nuclear magnetic resonance spectra of BOSM in deuteriochloroform (Figure 4) displays a distorted triplet at  $\delta$  0.88 and an intense singlet at  $\delta$  1.31 which are characteristic of the n-octyl methylene and methyl protons. The triplet observed at  $\delta$  2.95 is attributable to the n-octyl methylene protons adjacent to the sulfoxide group. The isolated methylene protons are manifested as the singlet at  $\delta$  3.94 and the doublet centered at  $\delta$  3.93 ( $J = 20 \text{ cps.}$ ). The singlet is believed to correspond to the dl configuration of the bis sulfoxide whereas the doublet is believed to arise from the unequivalent methylene protons of the meso configuration (63). The proton integration gives a ratio of 6.0 : 23.0 : 3.8 : 1.9 for  $(\text{CH}_3)_2$  :  $[(\text{CH}_2)_6]_2$  :  $(\text{CH}_2\text{SO})_2$  :  $\text{SOCH}_2\text{SO}$ . The ratio of meso to dl appears to be approximately unity.

A sulfur-oxygen analysis of the compound, performed by M-H-W Laboratories, gave 10.04% oxygen and 17.31% sulfur compared to the

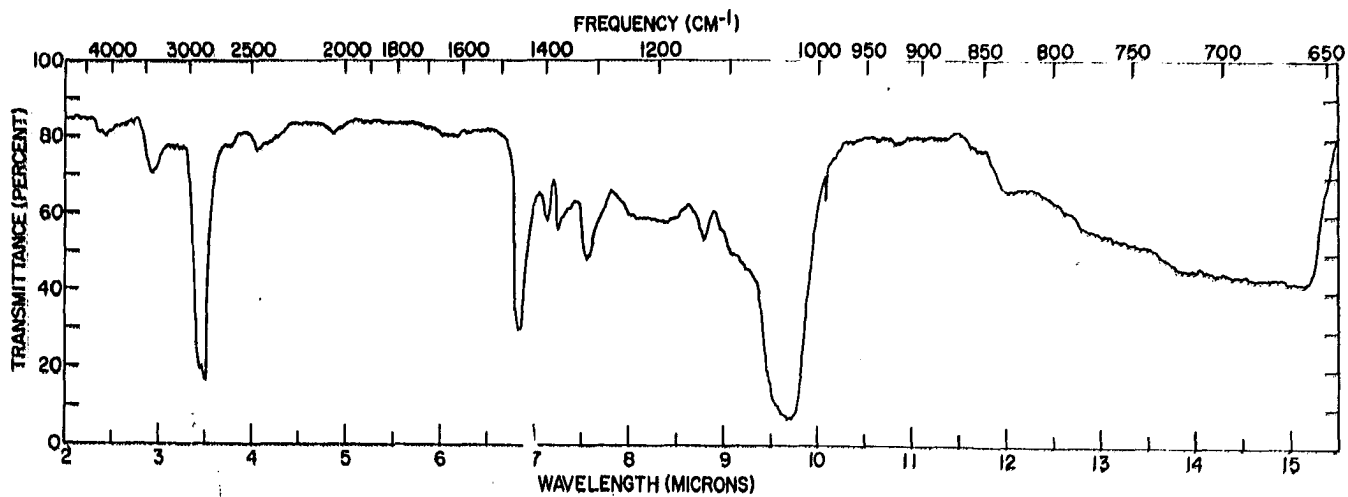


Figure 3. The infrared absorption spectrum of bis(n-octylsulfinyl)methane in chloroform

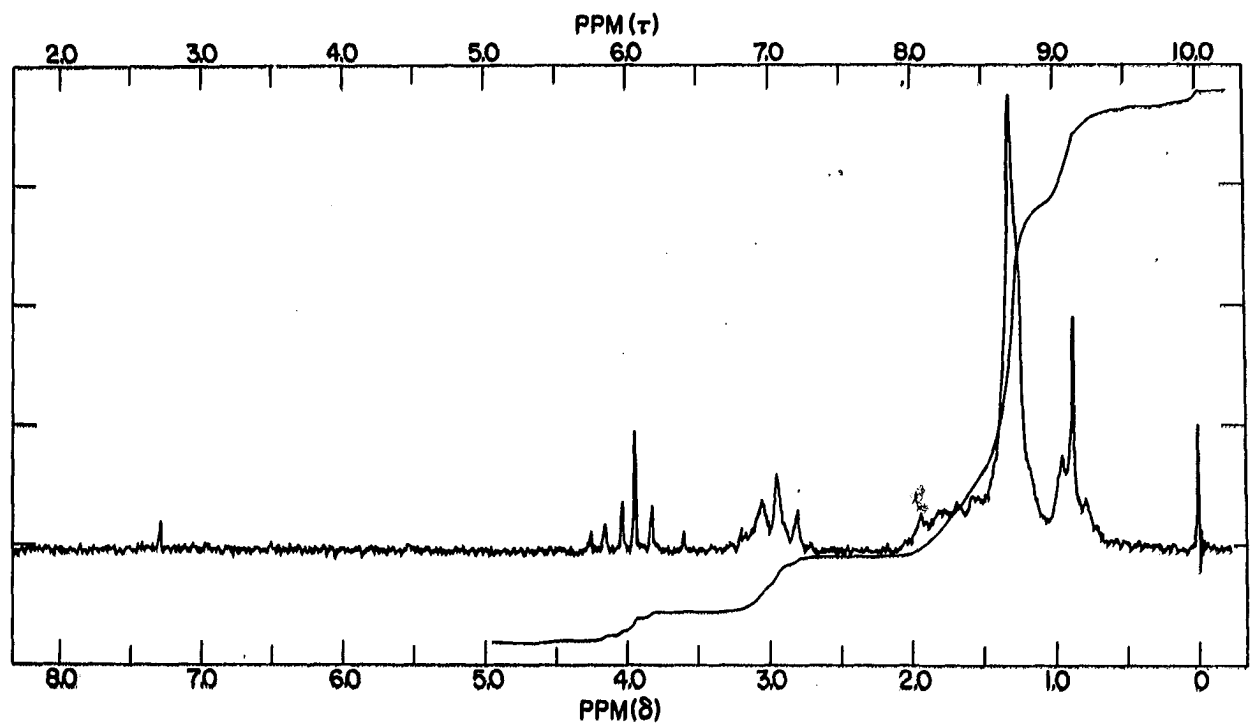


Figure 4. The nuclear magnetic resonance spectrum of bis(n-octylsulfinyl)methane in deuteriochloroform

theoretical values of 9.56% oxygen and 19.17% sulfur. The higher than stoichiometric amount of oxygen indicates some sulfone impurity.

bis(*n*-Octylsulfinyl)ethane (BOSE)

The corresponding sulfide was first prepared by refluxing *n*-octyl bromide for two hours with a 10% excess of 1,2-dimercaptoethane in the presence of ethanolic potassium hydroxide. The product was purified by extracting several times with aqueous sodium hydroxide solution followed by extractions with water. The sulfide was dried over anhydrous sodium sulfate and then oxidized with hydrogen peroxide using the procedure described for BOSM. Following the oxidation, the volume of acetic acid was reduced under vacuum and a quantity of crystals were isolated which were shown by their infrared spectra to contain large amounts of sulfone impurity. A large quantity of water was then added to the remaining solution and the solid product which formed was filtered, washed, and air dried. The crude bis sulfoxide was purified by fractional crystallization from ethanol. Those fractions which, from their infrared spectra, were shown to contain little or no sulfone impurity were combined, dissolved in ethanol, and recrystallized. The final product, a white solid in the form of light, plate-like crystals, melted in the range 132.5 - 133.5° C.

The mass spectra revealed only a small peak at  $m/e$  350 corresponding to the molecular weight of the parent ion of the bis sulfoxide. In the fragmentation pattern, however, several strong peaks were observed at  $m/e$  intervals corresponding to ions resulting from the unsymmetrical cleavage of the bis sulfoxide. For example, the peak at  $m/e$  237, which



appears to contain two sulfur atoms (as inferred from the  $m/e$  239 peak), corresponds to the ion  $C_8H_{17}SOCH_2CH_2SO^+$ .

The infrared spectra of BOSE in chloroform (Figure 5) displays a strong absorption peak centered at  $1021\text{ cm.}^{-1}$  indicative of the presence of the sulfoxide group. Two weak absorption peaks are observed at  $1132\text{ cm.}^{-1}$  and  $1318\text{ cm.}^{-1}$  suggesting the presence of a small amount of sulfone impurity.

The NMR spectra of BOSE in deuteriochloroform (Figure 6) shows essentially the same pattern for the n-octyl methylene and methyl protons as that described for BOSM. The distorted triplet, centered at  $\delta 2.79$  is interpreted as arising from the n-octyl methylene proton adjacent to the sulfoxide group. The complex pattern centered at  $\delta 3.11$ , which has been expanded to reveal more details, is attributed to the isolated methylene groups. This is compatible with the complicated splitting expected from the AA'BB' system present in the anticipated mixture of diastereomers (63). The proton integration gives a ratio of 3.0 : 12.6 : 2.0 : 1.9 for  $CH_3$  :  $(CH_2)_6$  :  $CH_2SO$  :  $CH_2$ .

A sulfur-oxygen analysis of BOSE gave 18.30% sulfur and 9.92% oxygen compared to the theoretical values of 18.40% sulfur or 9.18% oxygen. The higher than stoichiometric amount of oxygen indicates some sulfone impurity.

#### Di-n-octyl sulfone

Di-n-octyl sulfoxide was oxidized with an excess of hydrogen peroxide in glacial acetic acid. The product was precipitated by adding water and was filtered, washed and air dried. An infrared spectra of the

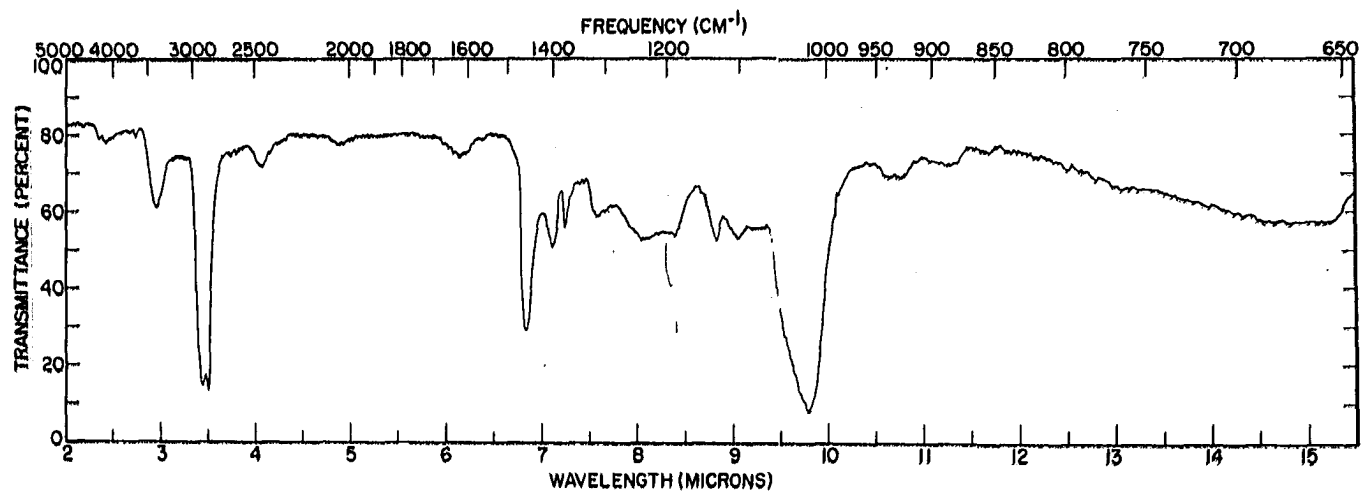


Figure 5. The infrared absorption spectrum of bis(n-octylsulfinyl)ethane in chloroform

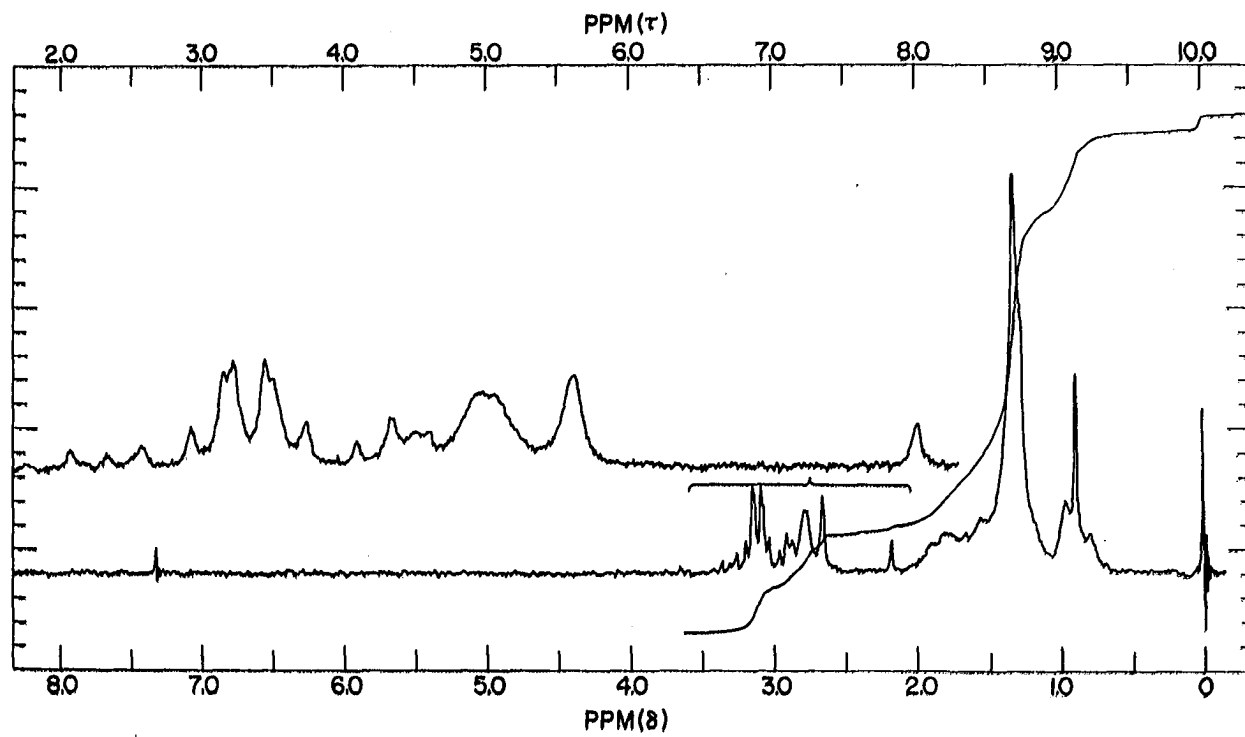


Figure 6. The nuclear magnetic resonance spectrum of bis(n-octylsulfinyl)ethane in deuteriochloroform

compound in chloroform revealed very intense sulfone absorption peaks at  $1130\text{ cm.}^{-1}$  and  $1318\text{ cm.}^{-1}$ . No sulfoxide absorption could be observed. The melting point of the compound,  $76 - 77^{\circ}\text{ C.}$  corresponds well to the literature value (44).

#### Paper Chromatography Survey

The results of the paper chromatography survey will now be discussed. The purpose of this discussion will be threefold:

1. To elucidate the nature of sulfoxide-metal interactions.
2. To compare the extraction behavior of sulfoxides with each other and with the phosphoryl extractants.
3. To point out the existence of potential separation systems.

#### Di-n-octyl sulfoxide - hydrochloric acid

The chromatographic behavior of metals on paper impregnated with DOSO and eluted with 1-10 M hydrochloric acid is presented in Figure 7.

Strong extraction is seen for those metals which are known to form strong chloride complexes (36, 64) such as iron(III), gallium(III), gold(III), tin(IV), mercury(II), molybdenum(VI), uranium(VI), etc. This indicates that, as expected, extraction takes place through the mechanism of solvation of a neutral, chloride complex.

As noted in a previous section, the anion exchange behavior of iron(III), antimony(V), tin(IV), gold(III), molybdenum(VI), and uranium(VI) in DMSO-hydrochloric acid was interpreted as resulting from strong solvation of these metals by DMSO. Likewise, these same metals are strongly solvated (and extracted) by DOSO. Tin(IV) and antimony(V) were

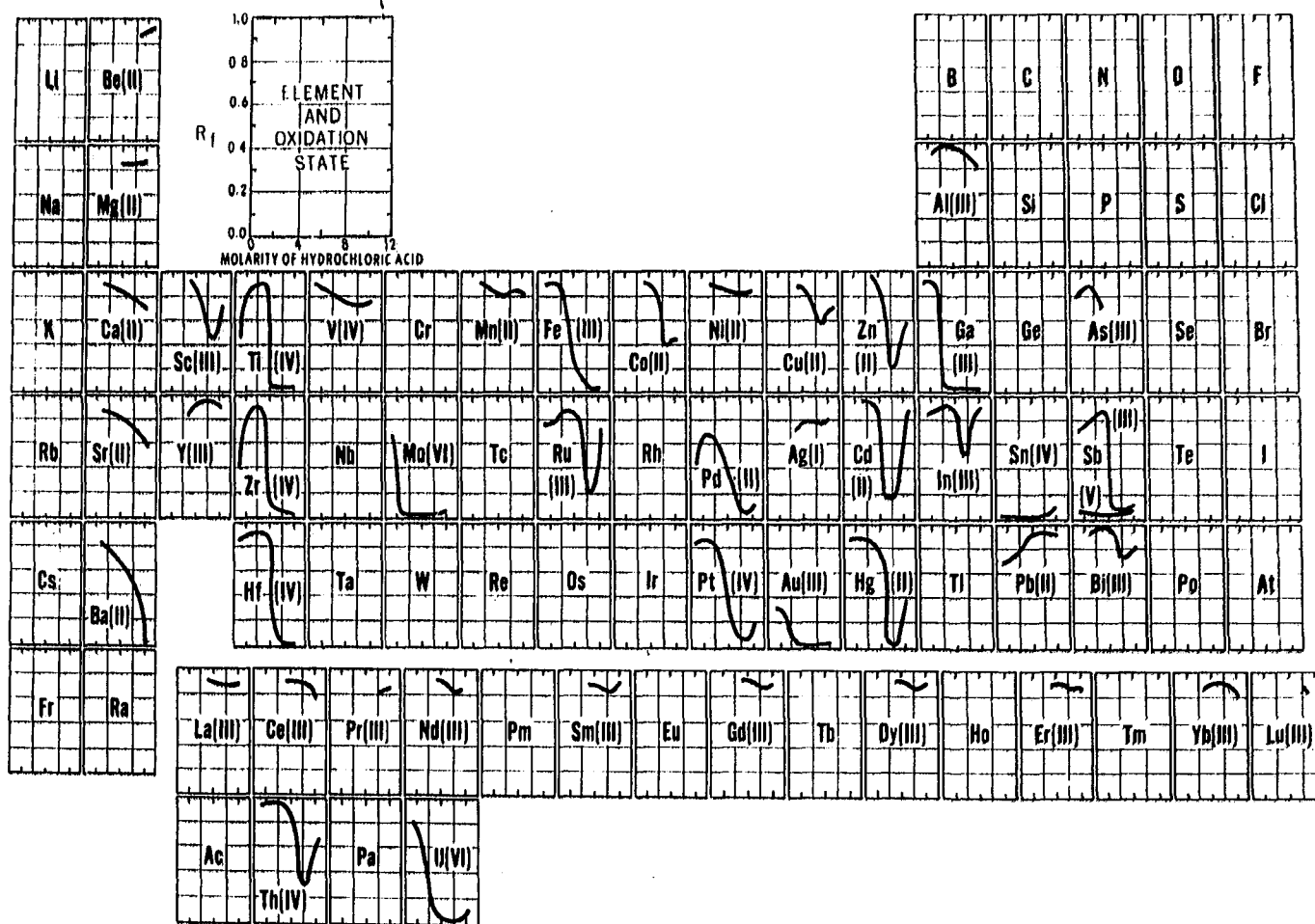


Figure 7. The chromatographic behavior of metal ions on paper impregnated with di-n-octyl sulfoxide eluted with hydrochloric acid

also noted for the exceptional stability of their DMSO complexes. Significantly, these two metals are the most strongly extracted of all studied. Titanium(IV) was also mentioned as possessing a very stable DMSO complex. It will be seen that titanium(IV) is one of the few metals that is consistently more strongly extracted by the sulfoxides than by tri-n-octyl phosphine oxide (TOPO).

Palladium(II) and gold(III) are fairly strongly extracted by DOSO but more weakly so than with TOPO (9). Apparently, the expected mechanism of extraction of these metals--solvation of the metal through the sulfinyl sulfur atom--is of no practical advantage in this particular system.

Many metals are seen to go through an extraction maximum with increasing acid concentration. This phenomenon, observed throughout the work for all reagents and in all acid systems, is typical behavior for neutral, polar extractants. This decrease in extraction at higher acid concentrations is the result of the interaction of two independent phenomena;

1. The competitive extraction of mineral acids by the reagent.
2. The formation of unextractable, anionic, metal-chloride complexes, metal-nitrate complexes, etc.

The basicity of the reagent and the nature of the mineral acid determine the effect of 1, whereas the effect of 2 will be decided by the coordination properties of the metal.

It should be noted that the behavior of the group II A metals is not due to coordination by DOSO. Identical behavior is observed on "blank" chromatograms, indicating that the limited solubility of the heavier

alkaline earth chlorides in strong hydrochloric acid is responsible.

Compared with similar paper chromatography data for TOPO, DOSO is a generally weaker extractant. This is to be expected in light of the earlier discussion of the effect of dipole moments upon the extraction of metal complexes.

<u>Stronger than TOPO</u>	<u>Comparable</u>	<u>Weaker than TOPO</u>
Ti(IV)	Th(IV), Pd(II), Au(III), Mo(VI), Mn(II), Sn(IV), Sb(V), Ni(II), Co(II), Ag(I)	Sc(III), Zr(IV), Hf(IV), U(VI), Fe(III), Pt(IV), Hg(II), Zn(II), Cd(II), etc.

The data in Figure 7 suggest the possibility of many separations.

Some of the more significant ones are listed below.

1. Tin(IV) and antimony(V) can be separated from all other metals studied at 1 M hydrochloric acid.
2. Molybdenum(VI) can be separated from all metals at 2-3 M hydrochloric acid, except tin(IV) and antimony(V). Molybdenum(VI) can then be separated from these two metals at 1 M hydrochloric acid.
3. Gallium(III) can be separated from iron(III), aluminum(III), indium(III), and many other metals at 4-5 M hydrochloric acid.
4. A separation of zinc(II) and cadmium (II) from mercury (II) appears possible at 8 M hydrochloric acid.
5. Thorium(IV) can be separated from titanium(IV), zirconium(IV), hafnium(IV), and uranium(VI) at 8 M hydrochloric acid.

#### p-Tolyl sulfoxide - hydrochloric acid

The chromatographic behavior of metals on paper impregnated with

PTSO and eluted with 1-10 M hydrochloric acid is presented in Figure 8.

The same metals are extracted by PTSO as by DOSO, indicating that the mechanism is, again, solvation of a neutral, chloride complex. However, these metals are generally more weakly extracted by PTSO.

<u>Stronger than DOSO</u>	<u>Comparable</u>	<u>Weaker than DOSO</u>
Sc(III), Th(IV)	Mo(VI), Fe(III), Co(II), Ni(II), Cu(II), Ga(III), Au(III), Sb(V), Ti(IV), Zr(IV), Hf(IV)	Zn(II), Cd(II), Hg(II), Pd(II), Pt(IV), In(III), Ru(III), Sn(IV), U(VI)

Weaker extraction by PTSO is to be expected owing to ring inductive effects which tend to reduce the polarity of sulfur-oxygen bond, thus making PTSO a weaker donor. Likewise, the availability of the lone electron pair should be reduced resulting in decreased extraction of those metals postulated to coordinate through the sulfur atom. This decrease is observed for palladium(II), but not for gold(III).

That PTSO is a weaker extractant than DOSO does not lessen its potential usefulness as a reagent for separations. This can be an advantage in many situations because, as extractive power decreases, selectivity generally increases. The separation possibilities listed below illustrate this.

1. Antimony(V) can be separated from all other elements studied at 1 M hydrochloric acid.
2. Antimony(V) and gold(III) can be separated from all other elements studied at 4 M hydrochloric acid.
3. A separation of zirconium(IV) and hafnium(IV) appears likely at 8 M hydrochloric acid.



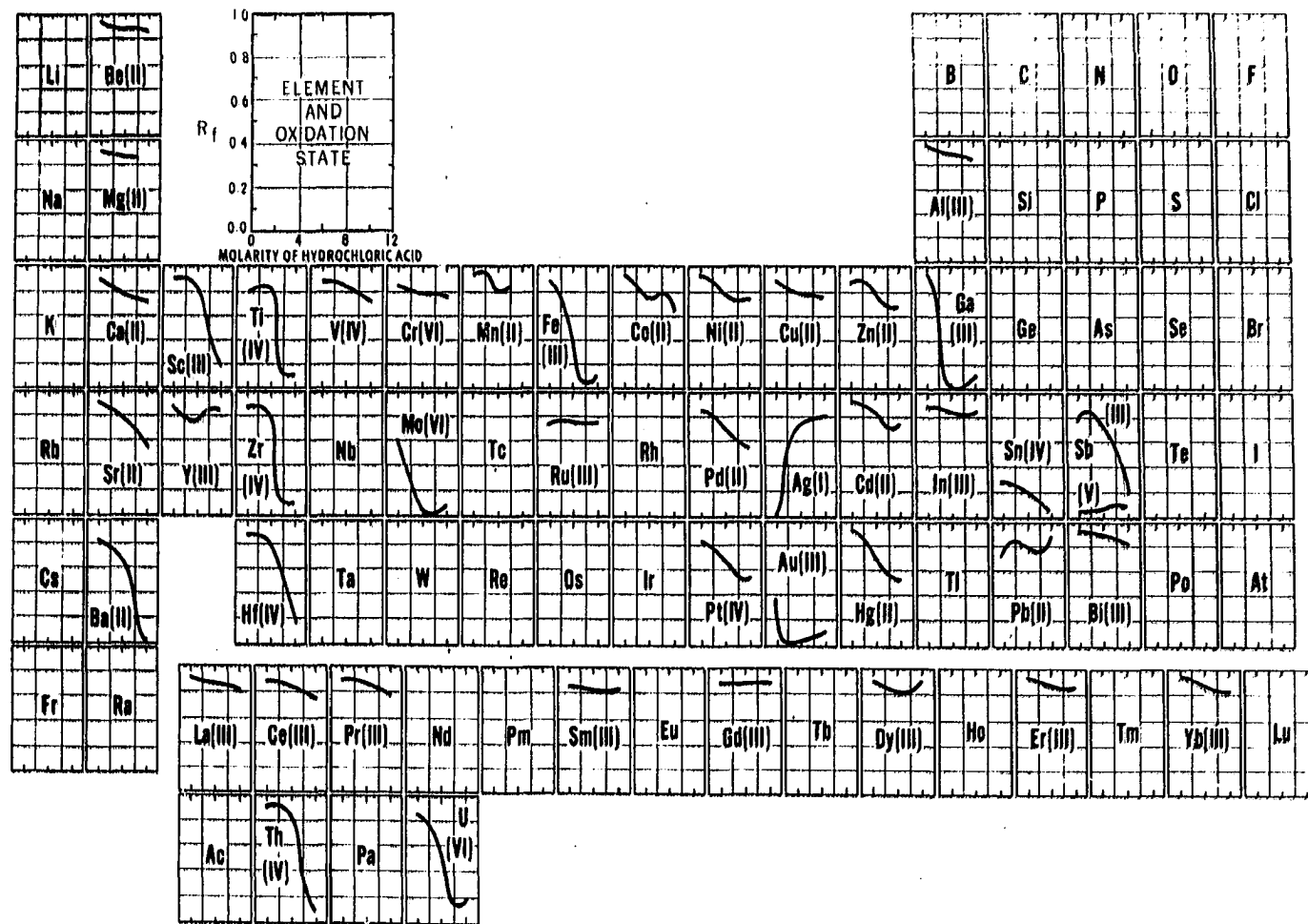


Figure 8. The chromatographic behavior of metal ions on paper impregnated with p-tolyl sulfoxide eluted with hydrochloric acid

bis(n-Octylsulfinyl)methane - hydrochloric acid

The chromatographic behavior of metals on paper impregnated with BOSM and eluted with 1-10 M hydrochloric acid is presented in Figure 9.

The extraction of metals from hydrochloric acid by BOSM is surprisingly weak. The superior coordinating properties which were anticipated for this material have not been realized. BOSM is a much weaker extractant than DOSO and, for the most part, even PTSO.

<u>Stronger than DOSO</u>	<u>Comparable</u>	<u>Weaker than DOSO</u>
Th(IV)	Sb(V), Sc(III)	U(VI), Ti(IV), Zr(IV), Hf(IV), Mo(VI), Fe(III), Ga(III), Pd(II), Pt(IV), Au(III), Zn(II), Cd(II), Hg(II), Sn(IV), etc.

A significant exception to the above generality is thorium(IV) which is extracted more strongly by BOSM than by DOSO, PTSO, or even TOPO. With BOSM, thorium(IV) is extracted more strongly than uranium(VI), whereas with the other three reagents, the reverse is true. Rationalization of the behavior of BOSM will be withheld until the discussion of the next reagent.

The anomalously strong interaction of thorium(IV) with BOSM suggests the following separation possibility: At 8-9 M hydrochloric acid thorium (IV) can be separated from uranium(VI), titanium(IV), zirconium(IV), hafnium(IV), lanthanides(III), scandium(III), etc. Only antimony(V), gallium(III), iron(III), and molybdenum(VI) are likely to interfere.

bis(n-Octylsulfinyl)ethane - hydrochloric acid

The chromatographic behavior of metals on paper impregnated with BOSE and eluted with 1-10 M hydrochloric acid is presented in Figure 10.

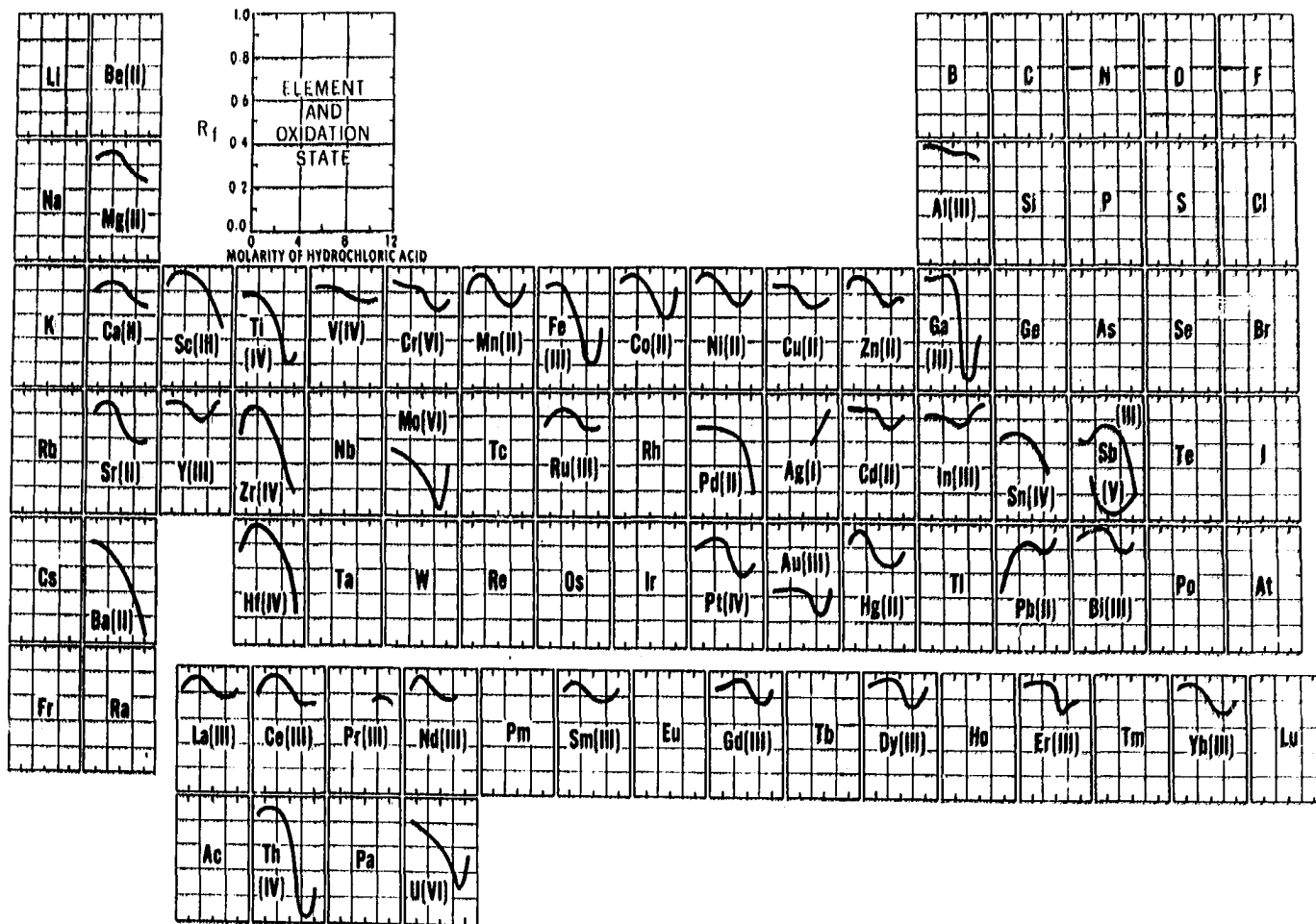


Figure 9. The chromatographic behavior of metal ions on paper impregnated with bis[(n-octyl sulfinyl] methane eluted with hydrochloric acid

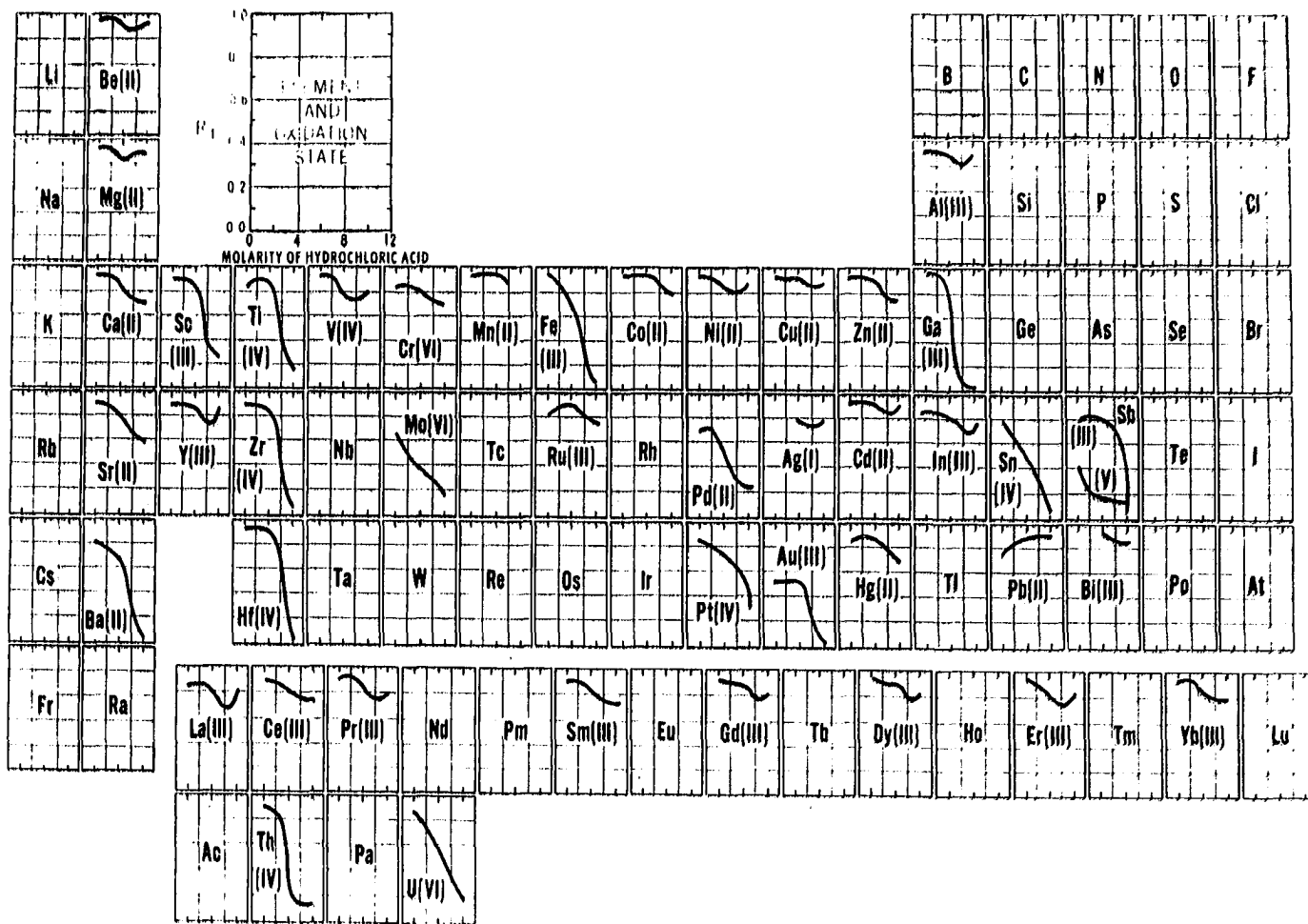


Figure 10. The chromatographic behavior of metal ions on paper impregnated with bis[n-octyl sulfinyl] ethane eluted with hydrochloric acid

The extraction of metals from hydrochloric acid by BOSE is, again, surprisingly weak. Like BOSM, BOSE is a weaker extractant than either DOSO or PTSO for all metals except thorium(IV). Significantly, however, BOSE is a notably stronger extractant than BOSM for a large number of metals.

<u>Stronger than BOSM</u>	<u>Comparable</u>	<u>Weaker than BOSM</u>
U(VI), Sc(III), Ti(IV), Zr(IV), Hf(IV), Fe(III), Ga(III), Sn(IV), Pt(IV), Au(III)	Pd(II), Hg(II), Co(II), Th(IV)	Mo(VI), Sb(V)

It has been observed that, unlike the analogous phosphoryl compounds, the first two members of the series of bis sulfoxides are not stronger extractants (with one exception) than the corresponding monofunctional sulfoxides. Furthermore, the first member of the series of bis phosphine oxides is a generally stronger extractant than the second whereas the reverse is true for the bis sulfoxides. An attempt will now be made to rationalize this behavior.

The weak extraction of the bis sulfoxides could be explained by simply postulating that these compounds extract as monodentate ligands. A more reasonable explanation, however, is that bidentate coordination occurs, but that the interaction is so ineffective as to be weaker than the coordination of monofunctional sulfoxides.

The existence of bidentate coordination cannot be ruled out simply on the basis of the observed, weak extraction. As was pointed out in an earlier section, the bis phosphine oxides do not usually display a significant advantage over monofunctional phosphine oxides when extraction occurs through the mechanism of solvation of a neutral metal-ligand

complex. The spectacular increase in extraction is only observed in situations which involve high extractant-metal ratios, such as in the extraction of uranium(VI) from perchloric acid and in the extraction of the lanthanides from nitric acid and perchloric acid. Thus, in the extraction of metal-chloride complexes, it is quite possible that weak bidentate coordination is responsible for observed behavior of the bis sulfoxides.

The weakness of bidentate coordination can be explained in terms of steric hindrance. Of all possible rotational forms, the most favorable molecular configuration for extraction is that in which both oxygen atoms are readily available for simultaneous coordination with the metal. This requires that the oxygen atoms be brought close together, the actual proximity being determined mainly by the size of the metal. From an examination of molecular scale models of the bis sulfoxides, it appears that this configuration should be difficult to attain owing to the repulsion of adjacent, lone electron pairs. The closer the oxygen atoms are brought together, the closer are the lone pairs to one another, and, thus, the greater the repulsion. This repulsion will make it energetically unfavorable for these molecules to exist in the proper configuration for bidentate coordination, thus weakening the metal-sulfoxide bonds. Furthermore, the repulsion should be strongest for BOSM where the sulfinyl groups are closest together. The insertion of an additional methylene group reduces steric hindrance with the result that BOSE is a more "limber" molecule. BOSE should be able to more easily attain the proper configuration, thus forming stronger complexes.

In the case of the bis phosphine oxides, lone pair repulsion is

absent and the first two members of the series are both apparently able to easily attain favorable extraction configurations. However, in this configuration, the first member of the series (MHDPO) now coordinates most strongly because the smaller distance between phosphoryl groups allows a closer proximity of the oxygen atoms to the metal. If lone pair repulsion were absent, sulfoxides should behave similarly.

From the above arguments, it follows that the bis sulfoxides should coordinate more easily with large ions than with small ones. Furthermore, BOSE should be more effective than BOSM chelating small ions. These conclusions are in agreement with the observed extraction behavior and with the data (65, 66) presented in Table 3.

Table 3. Ionic radii of some metal ions which form chloride complexes

Metal ion	Ionic radius (Angstroms)
Fe <sup>+3</sup>	0.53
Ga <sup>+3</sup>	0.60
Sc <sup>+3</sup>	0.68
Sn <sup>+4</sup>	0.71
Ti <sup>+4</sup>	0.60
Zr <sup>+4</sup>	0.74
Hf <sup>+4</sup>	0.75
Th <sup>+4</sup>	0.96
U <sup>+6</sup>	0.86

It will be recalled that all of these metals, except thorium(IV), are much more strongly extracted by DOSO than by either BOSM or BOSE. The anomalously strong extraction of thorium(IV) by the bis sulfoxides can now be explained. It is the only metal (which forms an extractable chloride complex) that is large enough to be really effectively chelated. It should also be pointed out that extraction by a chelation mechanism is especially advantageous in the case of thorium(IV) owing to its high coordination number of eight (65). Although uranium(VI) also has a rather large ionic radius, the uranyl ion also possesses an unusually low coordination number of four (65). Thus, in the presence of a complexing anion such as chloride or nitrate, extraction by a bidentate ligand is of no real advantage. Furthermore, extraction by DOSO is probably also favored by reduced steric hindrance. The two monofunctional extractant molecules and the two anions are able to coordinate in a trans-trans configuration around the uranyl ion, whereas, with one molecule of BOSM (or BOSE) and two anions, the coordination stereochemistry is necessarily cis-cis. It will also be recalled that all of the metals in Table 3, except thorium(IV), are more strongly extracted by BOSE than by BOSM. This seemingly reversed order of extraction is now reasonable in light of the smaller degree of steric hindrance in BOSE which allows more effective bidentate coordination of these smaller ions.

The phenomenon of steric hindrance in bis sulfoxides will be referred to in future discussions of the extraction behavior of these compounds.

#### Di-n-octyl sulfoxide - nitric acid

The chromatographic behavior of metals on paper impregnated with DOSO



and eluted with 1-11 M nitric acid is summarized in Figure 11.

Strong extraction is seen for those metals which are known to form strong nitrate complexes (36, 64) such as Ti(IV), Zr(IV), Hf(IV), Th(IV), U(VI), Ag(I), Bi(III), etc. The probable mechanism of extraction of these metals is one of solvation of a neutral nitrate complex by the sulfinyl oxygen. The same metals are also extracted by TOPO although the interaction is, with one exception, stronger than that of DOSO. This is reasonable in view of the higher polarity of the phosphoryl bond. The anomalously high extraction of titanium(IV) by DOSO was also observed in hydrochloric acid systems. No explanation can be offered for this behavior.

<u>Stronger than TOPO</u>	<u>Comparable</u>	<u>Weaker than TOPO</u>
Ti(IV), Pd(II), Au(III), Sb(V)	Th(IV), U(VI), Bi(III), Mo(VI)	Sc(III), Y(III), Zr(IV), Hf(IV), Fe(III), Ag(I)

The strong extraction of palladium(II) and gold(III) by DOSO is significant. That these two metals, particularly palladium(II), are much more weakly extracted by TOPO is quite good evidence for sulfur-metal interaction in DOSO. The mechanism of extraction likely involves ion pair formation since palladium(II) does not form nitrate complexes. Such a mechanism would be favored by the low coordination number (four) of palladium(II). It is interesting that the extraction of palladium is stronger from nitric acid than from hydrochloric acid where, presumably, the mechanism of extraction is solvation of a neutral palladium-chloride complex. It may be that chloride ions compete with DOSO for coordination sites to form an unextractable, anionic complex.

It is probable that in the case of antimony(V) a chloride complex is

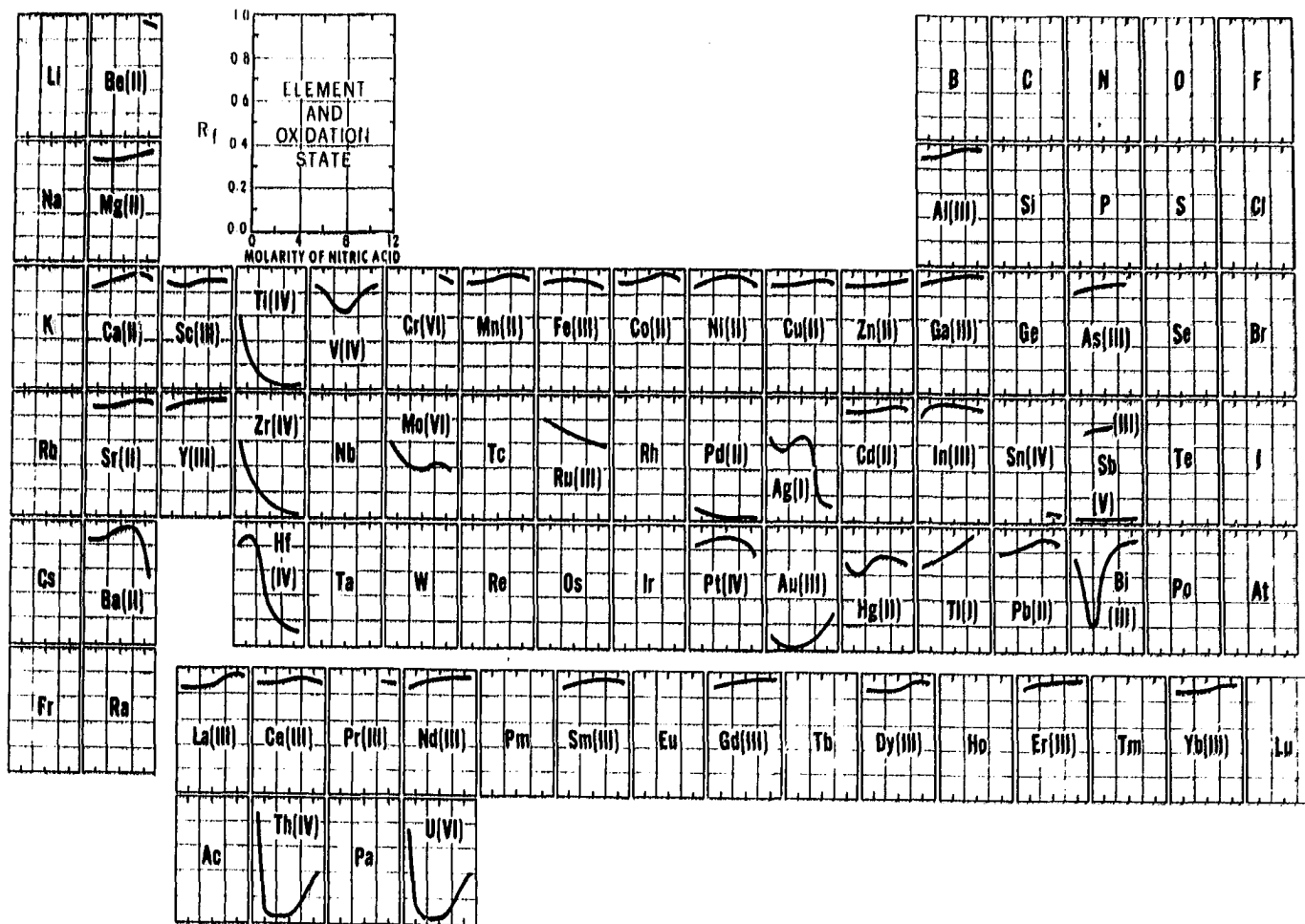


Figure 11. The chromatographic behavior of metal ions on paper impregnated with di-n-octyl sulfoxide eluted with nitric acid

being extracted. To prevent hydrolysis, this metal was applied to the paper in a fairly strong solution of hydrochloric acid. For this reason, the behavior of antimony(V) in nitric acid systems will not be further considered.

The data in Figure 10 suggest a number of useful separations, several of which are listed below.

1. A promising separation of zirconium(IV) and hafnium(IV) is seen at 4-8 M nitric acid.
2. Palladium(II) and gold(III) can be separated from all other metals studied, including platinum(IV), mercury(II), and silver(I), at 1 M nitric acid.
3. Thorium(IV) and uranium(VI) can be separated at 2 M nitric acid from most metals studied. Gold(III) and palladium(II) will interfere.
4. Titanium(IV), zirconium(IV) and hafnium(IV) at 11 M nitric acid can be separated from thorium(IV), uranium(VI) and most other metals studied. Palladium(II) and probably gold(III) will interfere.

#### p-Tolyl sulfoxide - nitric acid

The paper chromatographic behavior of metals on paper impregnated with PTISO and eluted with 1-11 M nitric acid is presented in Figure 12.

As expected, PTISO is observed to be a generally weaker extractant for those metals which form nitrate complexes. Likewise, palladium(II) and gold(III) are also more weakly extracted.

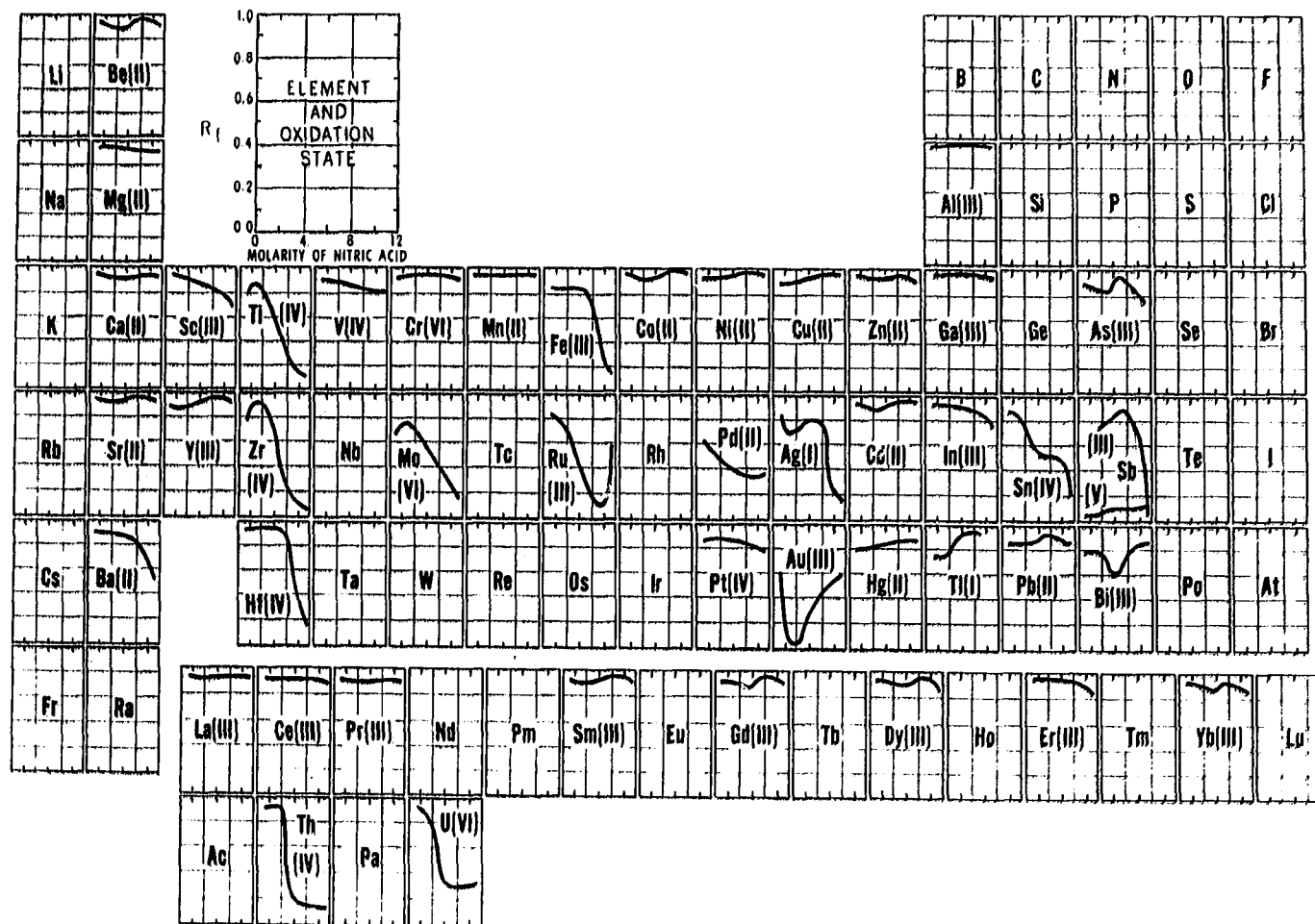


Figure 12. The chromatographic behavior of metal ions on paper impregnated with p-tolyl sulfoxide eluted with nitric acid

<u>Stronger than DOSO</u>	<u>Comparable</u>	<u>Weaker than DOSO</u>
Fe(III), Ru(III), Mo(VI)	Ag(I)	Ti(IV), Zr(IV), Hf(IV), Th(IV), U(VI), Bi(III), Au(III), Pd(II)

The strong interaction of PTISO with iron(III) and ruthenium(III) was completely unexpected and is of special interest. PTISO extracts these metals from nitric acid much more strongly than DOSO or even TOPO. The greatly enhanced interaction of the aromatic sulfoxide over the aliphatic sulfoxide suggests that the extraction may involve, in part, the formation of a  $\pi$ -complex with the aromatic rings. Although no analogous systems have been studied, this hypothesis is not unreasonable in view of the known tendency of iron(III) and ruthenium(III) to form  $\pi$ -complexes (e.g. ferrocene, ruthenocene, etc.) (67).

It is not advisable with the information now available to postulate structures for the extractable complexes. It will have to be determined if either the sulfinyl oxygen atom or the lone electron pair is involved in the bonding. One or the other (or both) of these interactions, in addition to  $\pi$ -bonding, seems likely. It is assumed that the extractions take place through a mechanism of ion pair association since iron(III) and ruthenium(III) do not form nitrate complexes. This view is supported by solvent extraction studies performed in perchloric acid which will be discussed in a later section.

Some useful separations using PTISO are listed below.

1. The unique extraction of iron(III) and ruthenium(III) at 10 M nitric acid will allow the separation of these metals from gallium(III), indium(III), aluminum(III), gold(III), platinum(IV),

bismuth(III), palladium(II), and uranium(VI).

2. Gold(III) is the only metal studied which is strongly extracted at 2-4 M nitric acid, thus, allowing a separation of gold(III) from 50 other metals.
3. A separation of zirconium(IV) and hafnium(IV) appears likely at 8-10 M nitric acid.

bis(n-Octylsulfinyl)methane - nitric acid

The chromatographic behavior of metals on paper impregnated with BOSM and eluted with 1-11 M nitric acid is presented in Figure 13.

As was observed for the hydrochloric acid system, BOSM is a generally weaker extractant than DOSO. There are a few exceptions, however, which support the hypothesis that BOSM extracts as a sterically hindered, bidentate ligand.

<u>Stronger than DOSO</u>	<u>Comparable</u>	<u>Weaker than DOSO</u>
Lanthanides(III), Ag(I), Ru(III)	Fe(III), Bi(III), Mo(VI)	Ti(IV), Zr(IV), Hf(IV), U(VI), Th(IV)

Fairly weak extraction is observed for the lanthanides. The extraction initially increases with atomic number, appears to go through a maximum near samarium or europium, and then decreases. That the lanthanides are extracted at all is indicative of bidentate coordination. The appearance of an extraction maximum is quite unexpected. A rationalization of this phenomenon in terms of steric hindrance will be included in the discussion of the behavior of BOSE in nitric acid where the same type of interaction, although much stronger, is also observed.

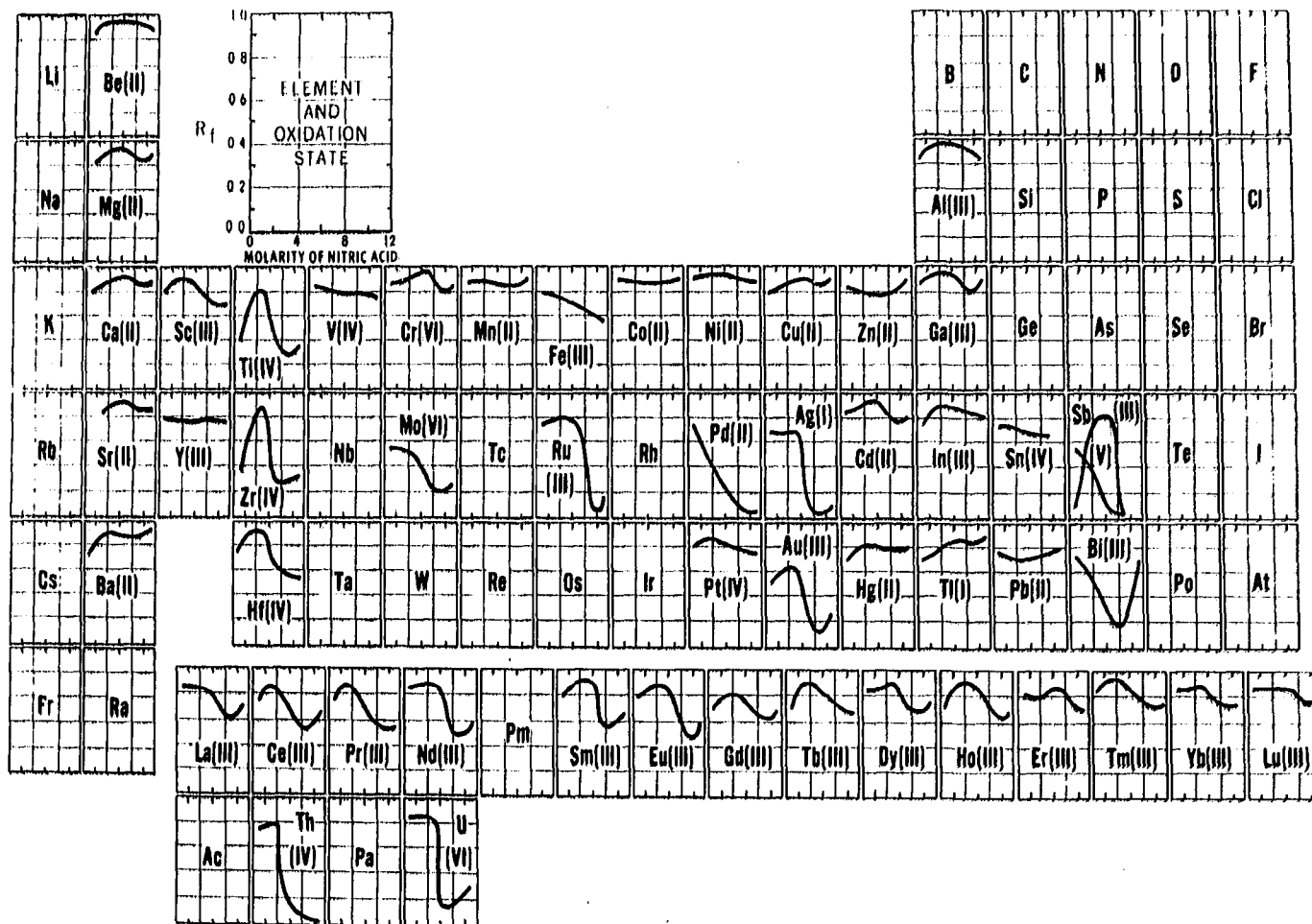


Figure 13. The chromatographic behavior of metal ions on paper impregnated with bis[*n*-octyl sulfinyl] methane eluted with nitric acid

Additional evidence of steric hindrance in bis sulfoxides is found in the extraction behavior of several other metals. Of all the ions which form nitrate complexes, silver(I) is the only one (other than the lanthanides) which is significantly more strongly extracted by BOSM than by DOSO. From the steric hindrance argument, this is not surprising in view of the large ionic radius of silver(I).

Table 4. Ionic radii of some metals which form nitrate complexes

Metal ions	Ionic radius (Angstroms)
Ag <sup>+</sup>	1.13
Bi <sup>+3</sup>	1.08
La <sup>+3</sup>	1.06
Y <sup>+3</sup>	0.96
Th <sup>+4</sup>	0.96
U <sup>+6</sup>	0.86
Lu <sup>+3</sup>	0.85
In <sup>+3</sup>	0.81
Hf <sup>+4</sup>	0.75
Zr <sup>+4</sup>	0.74
Sc <sup>+3</sup>	0.68
Ti <sup>+4</sup>	0.60

Similarly, bismuth(III), which also forms a nitrate complex, is equally strongly extracted by either BOSM or DOSO. The extraction of thorium(IV) from nitric acid by BOSM is weaker than the extraction by DOSO. That the



reverse was seen in hydrochloric acid does not invalidate the arguments for steric hindrance. It should be noted that the decrease in the extraction of thorium(IV) (going from DOSO to BOSM) is much less than that of titanium(IV), zirconium(IV), hafnium(IV) and uranium(VI). This indicates that the larger thorium(IV) is again more strongly solvated by BOSM than are the smaller ions. Apparently, the greater bulk of the nitrate ion (compared to the chloride ion) enhances steric hindrance effects so that coordination is especially favorable for metals of small charge, low coordination number, and large radius, such as silver (I).

The unusually strong extraction of ruthenium(III) by BOSM is quite unexpected. No rationalization of this phenomenon can be offered at this time.

Only one potential separation is of interest. At 10 M nitric acid, BOSM can be used to separate silver(I), palladium(II), ruthenium(III), and thorium(IV) from all other metals studied.

#### bis(*n*-Octylsulfinyl)ethane - nitric acid

The chromatographic behavior of metals on paper impregnated with BOSE and eluted with 1-11 M nitric acid is presented in Figure 14.

The very strong interaction of BOSE with a large number of metals is immediately apparent. Compared to DOSO, BOSE is a stronger extractant in many instances.

<u>Stronger than DOSO</u>	<u>Comparable</u>	<u>Weaker than DOSO</u>
Lanthanides(III), Sc(III), Y(III), Bi(III), Fe(III), Ru(III), Mo(VI)	V(IV), Ag(I)	Ti(IV), Zr(IV), Hf(IV), Th(IV), U(VI), Pd(II), Au(III)

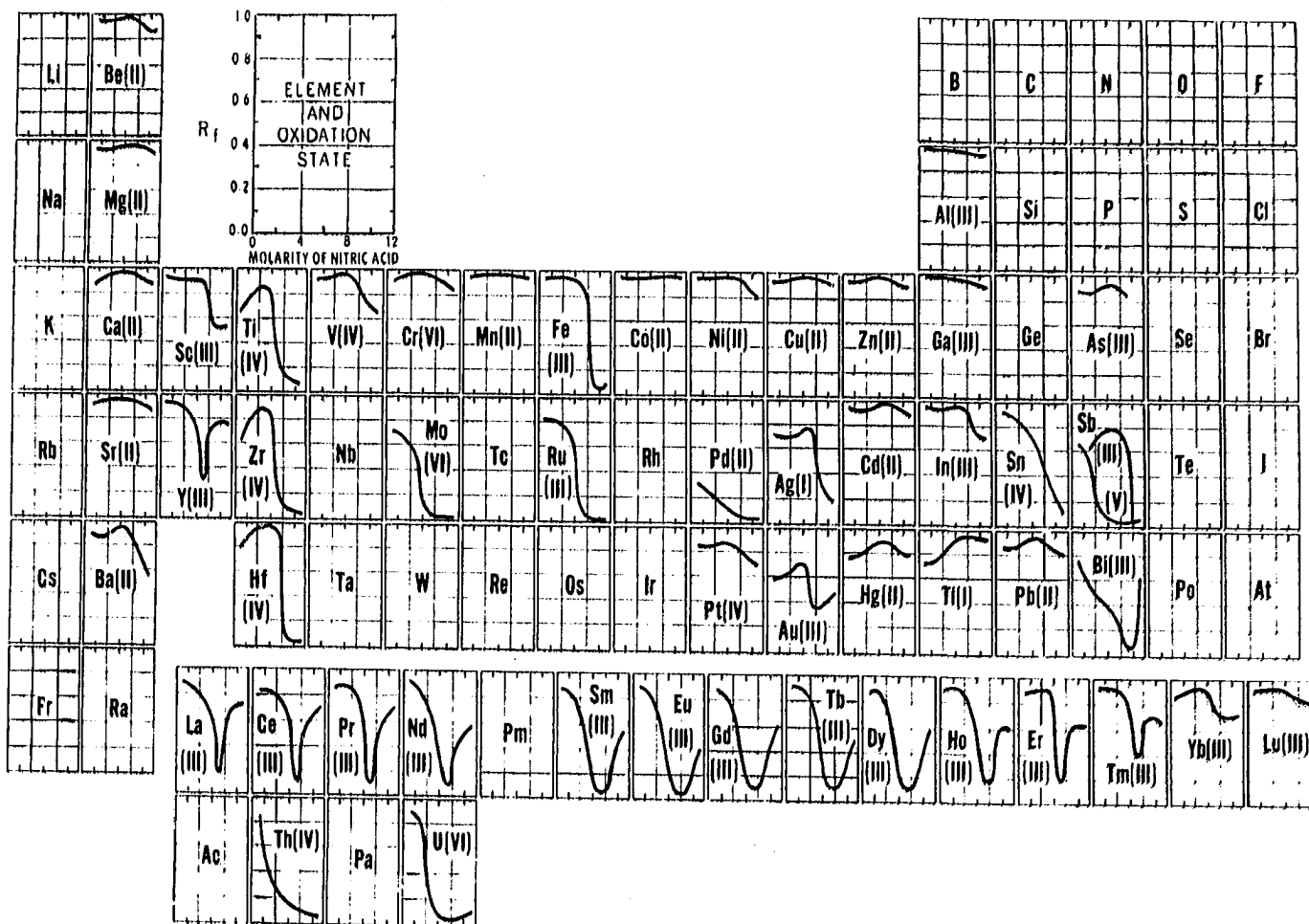


Figure 14. The chromatographic behavior of metal ions on paper impregnated with bis[n-octyl sulfinyl] ethane eluted with nitric acid

BOSE is a much stronger extractant than BOSM for all but a few metals.

<u>Stronger than BOSM</u>	<u>Comparable</u>	<u>Weaker than BOSM</u>
Lanthanides(III), Sc(III), Y(III), Bi(III), Ti(IV), Zr(IV), Hf(IV), V(IV), Fe(III), Ru(III), Pd(II)	Sb(III)	Ag(I), Au(III)

The extraction of metals which form nitrate complexes again confirms that, owing to reduced steric hindrance, BOSE is more effective in solvating small ions than is BOSM. Only silver(I), the largest ion listed in Table 4, is extracted more strongly by BOSM than by BOSE.

The most notable feature of Figure 13 is the strong extraction of the lanthanides. The moderately strong extraction at lanthanum(III) increases with atomic number, clearly passes through a maximum between samarium(III) and europium(III), and then decreases until at lutecium(III) the interaction is nearly non-existent. The same data are replotted in Figure 15 as distribution ratios to better illustrate the extraction behavior. The existence of a maximum in the extraction of the lanthanides by BOSE (and also by BOSM) is very significant. It constitutes the most straightforward demonstration yet discovered of steric hindrance effects in extractions with bis sulfoxides.

No such maximum is observed in the extraction of the lanthanides from nitric acid by the bis phosphine oxides. Analogous paper chromatography data for MHDPO (35) reveals a fairly steady increase in extraction from lanthanum(III) to lutecium(III). This is the behavior expected for a bidentate, neutral donor. The strength of the donor-metal bonds

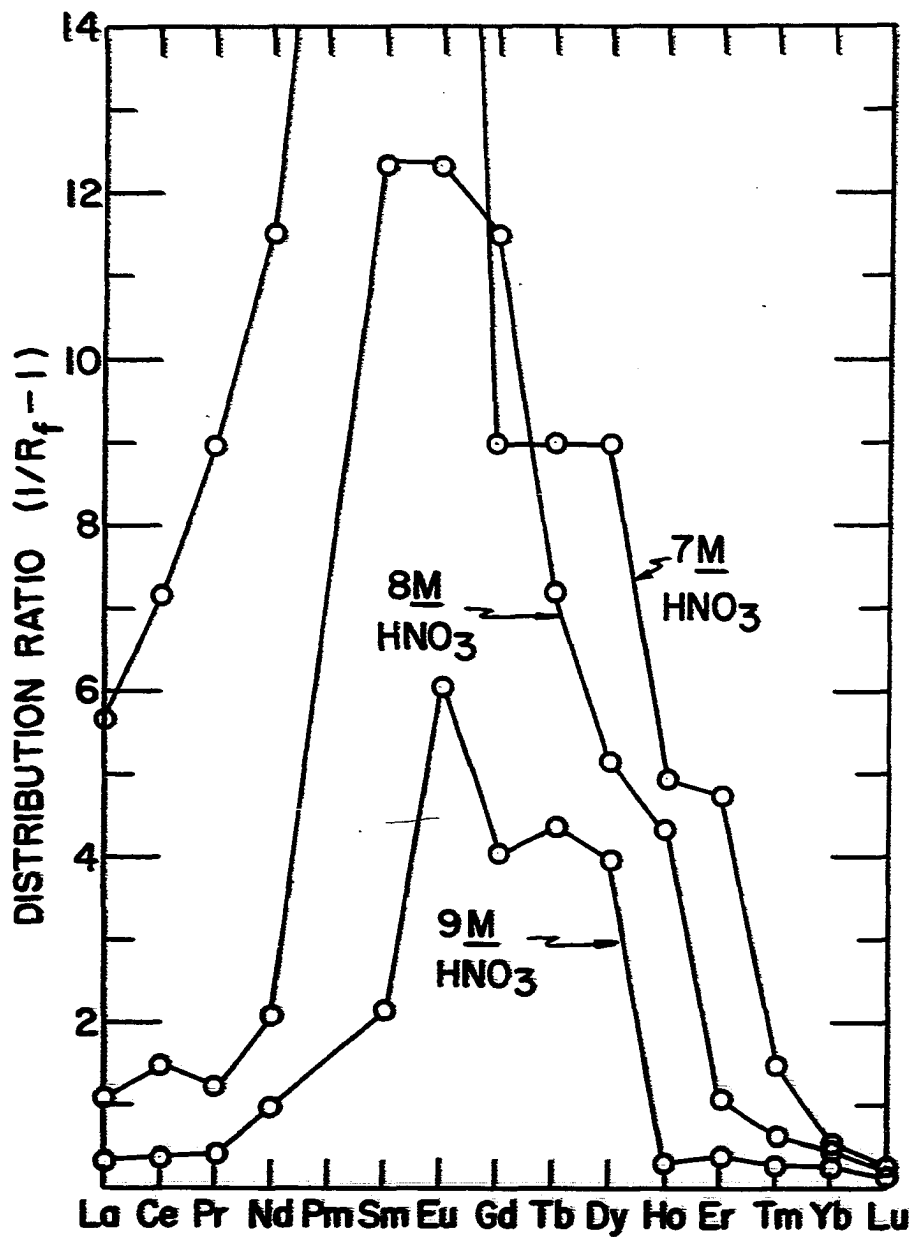


Figure 15. The chromatographic behavior of the lanthanides on paper impregnated with bis[*n*-octyl sulfinyl]ethane eluted with nitric acid

increases from lanthanum(III) to lutecium(III) as the ionic radii decrease, owing to the higher charge density of the smaller ions. At the same time, the stability constants of the lanthanide-nitrate complexes show a small but general decrease from lanthanum(III) to lutecium(III) (68, 69). However, this slight decrease in stability is completely overshadowed by the increasing bond strength resulting in increasing extraction with atomic number.

The same trend should occur for bis sulfoxides except that steric hindrance inhibits the chelation of the smaller lanthanide ions. For

Table 5. Ionic radii of trivalent lanthanide ions (65)

Element	Radius (Angstroms)
La	1.06
Ce	1.03
Pr	1.01
Nd	1.00
Pm	0.98
Sm	0.96
Eu	0.95
Gd	0.94
Tb	0.92
Dy	0.91
Ho	0.89
Er	0.88
Tm	0.87
Yb	0.86
Lu	0.85

the larger lanthanide ions, chelation occurs apparently without difficulty and extraction increases as the strength of metal-sulfoxide bonds with decreasing ionic radius. At europium(III), the ionic radius is apparently near the minimum value possible for unhindered chelation. Beyond

europium(III), the ability to chelate (and, hence, the ability to extract) is gradually lost with decreasing ionic radius. It is interesting that the ionic radius of europium(III) is very close to that of thorium(IV) (0.96 Angstroms) which was exceptionally strongly extracted by BOSE from hydrochloric acid.

Although similar behavior has not been observed for an analogous, single ligand, there are mixed ligand systems which do behave similarly. The extraction of the lanthanides by mixtures of thenoyltrifluoroacetone and tri-*n*-butylphosphate also passes through a maximum (70). This behavior has likewise been attributed to steric hindrance. Although the heaviest lanthanides should form the strongest complexes, these ions, owing to their small size, cannot accommodate the large number of ligands required (three of each) and the ability to extract is lost.

The combining ratio of BOSE with several lanthanide ions was determined using the paper chromatography loading technique. The metals were chromatographed in 8 M nitric acid on papers which had been impregnated with varying amounts of BOSE. Figure 16 shows a typical plot (europium(III)) of log distribution ratio as a function of the molar concentration of BOSE applied to the paper. Table 6 gives the slopes obtained for the five metals studied. From the earlier discussion of the theory of chromatography, the slopes indicate that the combining ratio of BOSE with these metals is 1 : 1.

The very strong extraction of iron(III) and ruthenium(III) is unexpected and cannot be explained on the basis of the information now available. Unfortunately, no analogous studies have been made with the bis phosphine oxides.

Figure 16. The paper chromatographic behavior of europium(III) eluted with 8 M nitric acid as a function of the molarity of bis[n-octylsulfinyl]ethane applied to the paper

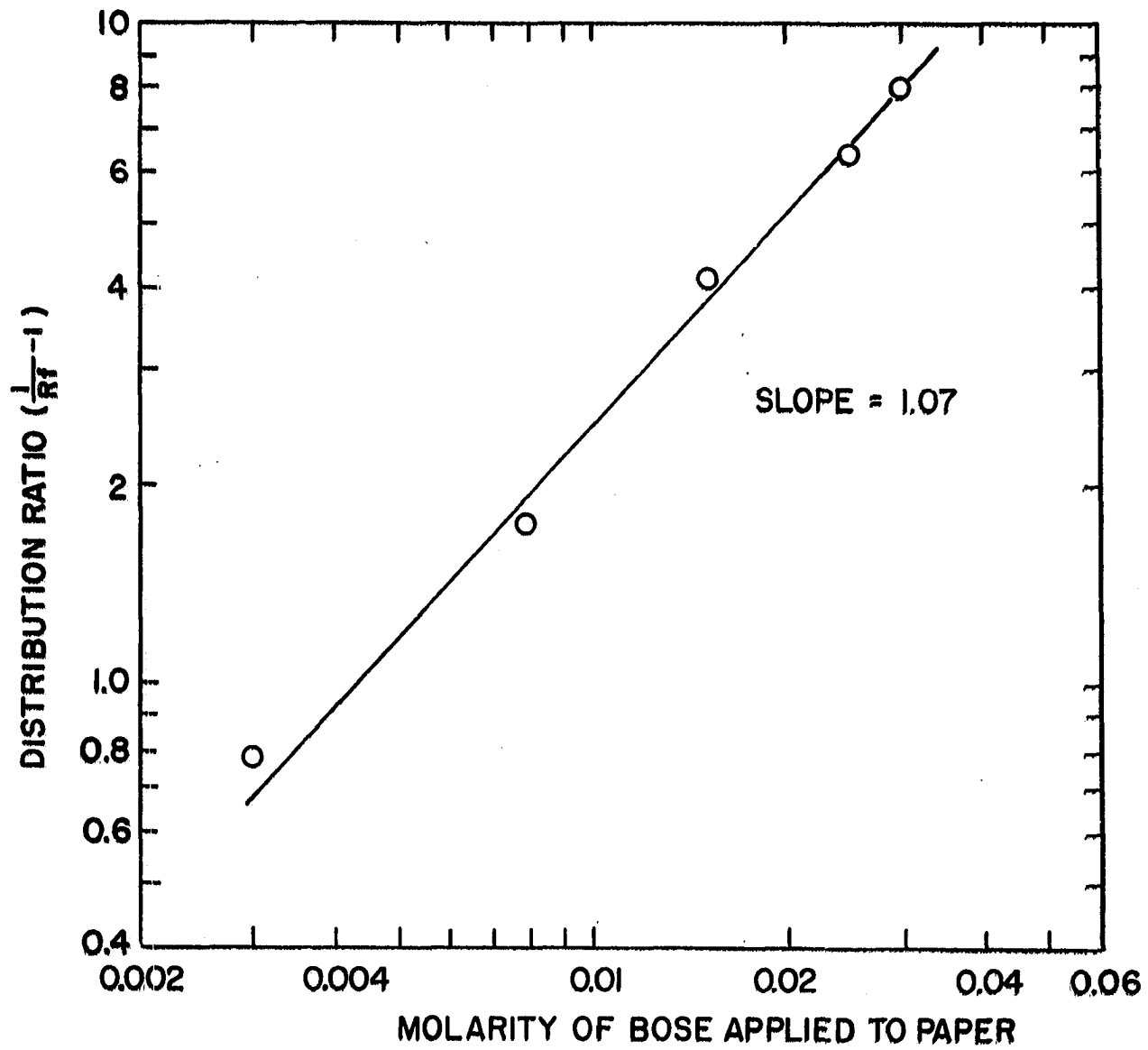




Table 6. Determination of the combining ratio of BOSE with some lanthanide ions

Metal	Slope
Samarium(III)	1.01
Europium(III)	0.99
Gadolinium(III)	1.01
Terbium(III)	0.95
Dysprosium(III)	0.97
Average value	0.99

The unique behavior of the lanthanide ions suggests a potentially useful separation. From Figure 14, it appears likely that at 7 M nitric acid, lanthanum(III) → erbium(III) can be separated from thulium(III) → lutecium(III). At 8-9 M nitric acid it should be possible to separate samarium(III) → dysprosium(III), including europium(III), from all other lanthanides. These separations, particularly the second, might be of some value on a preparative scale.

Di-n-octylsulfoxide - 1 M perchloric acid - ammonium thiocyanate

The chromatographic behavior of metals on paper impregnated with DOSO and eluted ammonium thiocyanate solutions containing 1 M perchloric acid is presented in Figure 17.

Strong and extensive extraction is seen for the many metals which form thiocyanate complexes (36, 64). Very strong extraction over the entire range of thiocyanate concentrations studied (0.02 - 2.0 M) is seen for titanium(IV), zirconium(IV), hafnium(IV), thorium(IV), uranium (VI), molybdenum(VI), and tin(IV). A number of other metals,

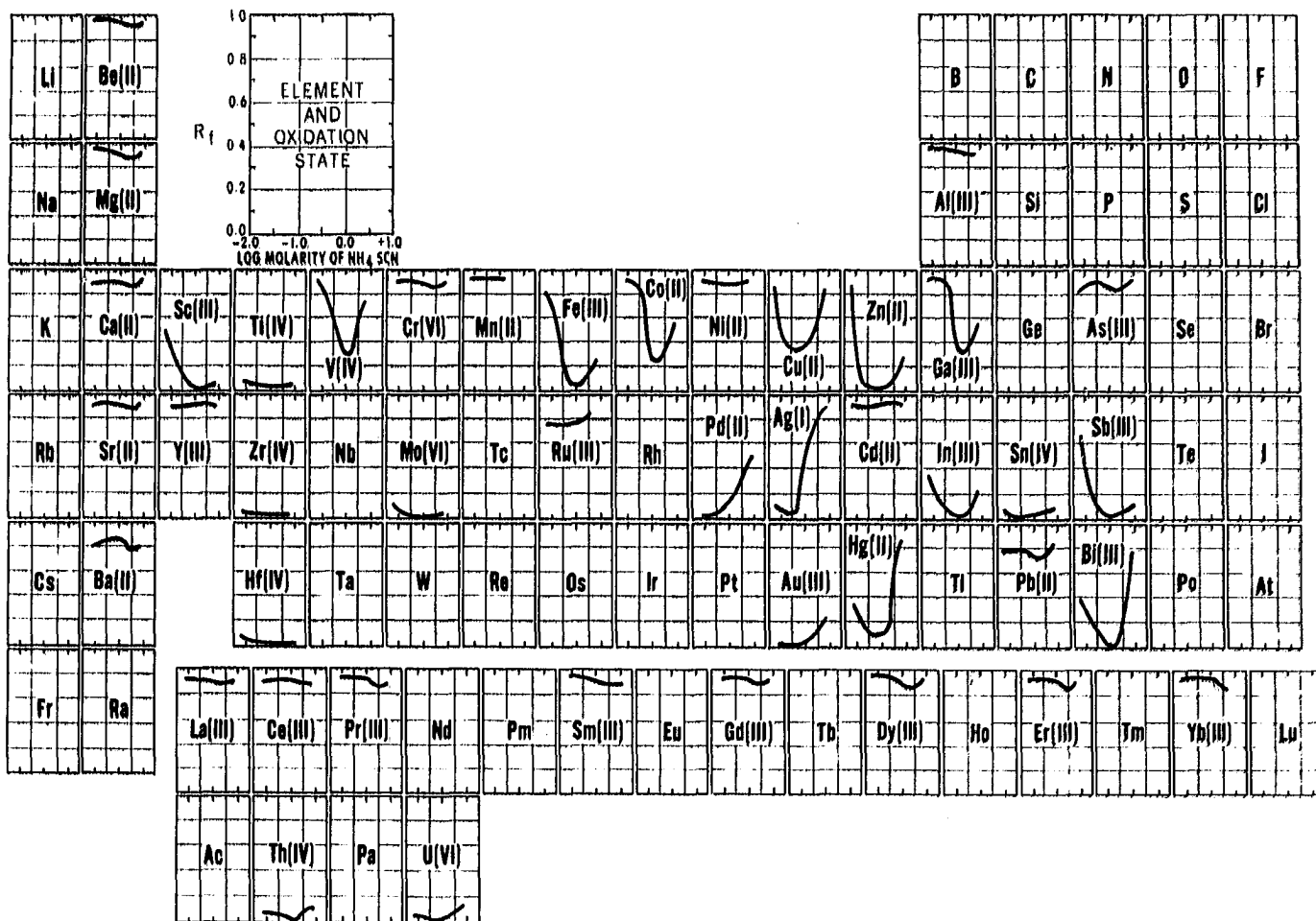


Figure 17. The chromatographic behavior of metal ions on paper impregnated with di-*n*-octyl sulfoxide eluted with 1 M HClO<sub>4</sub>-NH<sub>4</sub>SCN

scandium(III), iron(III), palladium(II), silver(I), gold(III), zinc(II), indium(III), and bismuth(III) are strongly extracted only at particular concentrations of thiocyanate. The decrease in extraction of these and other metals with increasing thiocyanate concentration is most probably the result of formation of higher, anionic thiocyanate complexes. The strong extraction of zinc(II) and mercury(II), but not of cadmium(II) is quite unusual as cadmium(II) also forms strong thiocyanate complexes. This phenomenon has been confirmed by solvent extraction studies and will be discussed in a future section. The behavior of scandium(III) and vanadium(IV) is also interesting. These metals have not been previously observed to be well extracted by any of the sulfoxides.

Unfortunately, no comparable set of data is available for the phosphine oxides. In light of previous comparisons, however, it seems certain that the extractions should be stronger, except perhaps for palladium(II) and gold(III).

Owing to the extensive and varied interactions of DOSO in thiocyanate media, a very large number of separations are possible. Some of the more interesting and useful ones are listed below.

1. Zinc(II) and mercury(II) can be easily separated from cadmium(II) at 0.2 M thiocyanate.
2. Iron(III), cobalt(II), and nickel(II) can be separated from each other at 0.6 M thiocyanate.
3. Aluminum(III), gallium(III), and indium(III) can be separated from each other at 0.3 M thiocyanate.
4. Copper(II), silver(I) and gold(III) can be separated from each other at 0.1-0.3 M thiocyanate.

5. Scandium(III) can easily be separated from yttrium(III), lanthanum(III)-lutectium(III), aluminum(III), gallium(III), etc. at 0.1 - 2.0 M thiocyanate.
6. In dilute thiocyanate solutions (about 0.02 M), the following metals can be separated from all others studied: titanium(IV), zirconium(IV), hafnium(IV), thorium(IV), tin(IV), uranium(VI), molybdenum(VI), palladium(II), gold(III), and silver(I).

bis(n-Octylsulfinyl)methane - 1 M perchloric acid - ammonium thiocyanate

The chromatographic behavior of metals on papers impregnated with BOSM and eluted with ammonium thiocyanate solutions containing 1 M perchloric acid is presented in Figure 18.

As was observed in all previous systems, BOSM is a generally weaker extractant than DOSO. The decrease in extraction is quite drastic for scandium(III), titanium(IV), zirconium(IV), thorium(IV), uranium(VI), zinc(II), and tin(IV). Table 7 compares the ionic radii of metals (65, 67) and the relative extent of their extraction by BOSM compared to DOSO.

Table 7. Comparison of ionic radii (Angstroms) of metals and their relative extent of extraction by BOSM and DOSO

Stronger than DOSO		Comparable		Weaker than DOSO	
Metal ion	radius	Metal ion	radius	Metal ion	radius
Cu <sup>+2</sup>	0.92	Hg <sup>+2</sup>	1.10	Zn <sup>+2</sup>	0.74
Cd <sup>+2</sup>	0.96	Bi <sup>+3</sup>	1.08	Sc <sup>+3</sup>	0.68
Ag <sup>+1</sup>	1.13	Sb <sup>+3</sup>	0.92	Ti <sup>+4</sup>	0.60

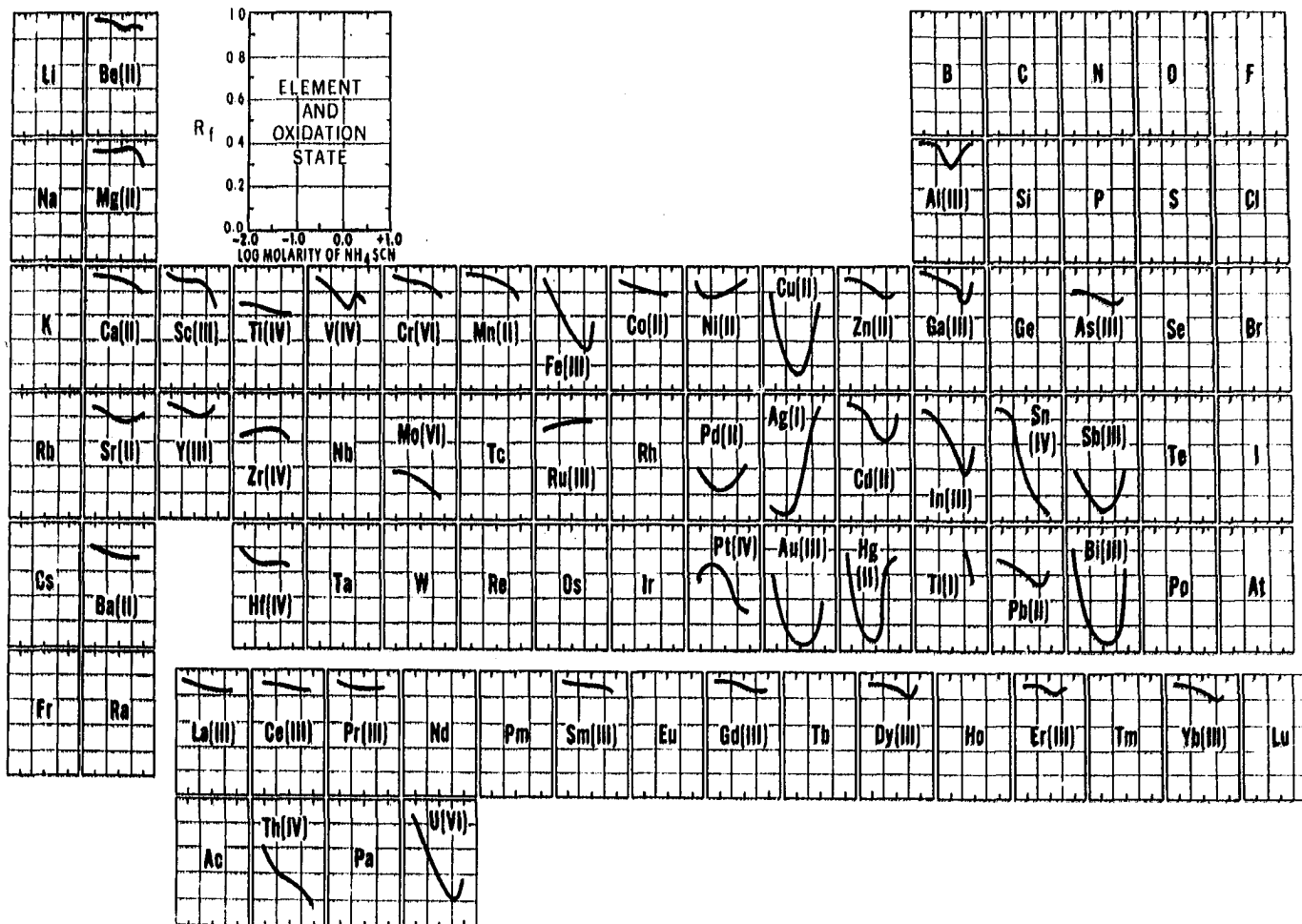


Figure 18. The chromatographic behavior of metal ions on paper impregnated with bis[n-octyl sulfinyl] methane eluted with 1 M  $\text{HClO}_4\text{-NH}_4\text{SCN}$

Table 7 (Continued)

Stronger than DOSO		Comparable		Weaker than DOSO	
Metal ion	radius	Metal ion	radius	Metal ion	radius
				Zr <sup>+4</sup>	0.74
				Hf <sup>+4</sup>	0.75
				Th <sup>+4</sup>	0.96
				U <sup>+6</sup>	0.86
				Sn <sup>+4</sup>	0.71
				Ga <sup>+3</sup>	0.60
				In <sup>+3</sup>	0.81
				Fe <sup>+3</sup>	0.53

Stronger solvation of larger ions is again observed and is further evidence of the existence of steric hindrance in bis sulfoxides. Of all the metals studied, only the behavior of thorium(IV) is drastically out of place. It is possible that the presence of the four, bulky thiocyanate ligands in the extractable thorium(IV) complex enhances the effect of steric hindrance.

A comparison of the extraction of zinc(II) and cadmium(II) by DOSO and BOSM is of special interest. It will be recalled that zinc(II) (radius = 0.74 Angstroms) was very strongly extracted by DOSO while cadmium(II) (radius = 0.96 Angstroms) was not extracted at all. The extraction of zinc(II) by BOSM is virtually nonexistent, whereas cadmium (II), although rather weakly extracted, is now more strongly extracted

than zinc(II). This reversal of the order of extraction of these two metals is additional evidence for the existence of a limiting radius for effective chelation.

The greatly decreased extraction of most metals by BOSM makes this reagent much more selective than DOSO. Two very useful separations are listed below.

1. In dilute thiocyanate solutions (about 0.02 M) silver(I) can be separated from all other metals studied.
2. Mercury(II) can be easily separated from zinc(II) and cadmium(II) at 0.1 - 0.3 M thiocyanate.

#### Di-n-octylsulfoxide - perchloric acid

The chromatographic behavior of metals on paper impregnated with DOSO and eluted with 0.01 - 6.0 M perchloric acid is presented in Figure 19.

Extraction from perchloric acid is limited, as predicted, to a very few metals, principally uranium(VI), palladium(II) and gold(III). The inability of the perchlorate ion to form inner sphere complexes requires that the strong extractions of these three metals occur through the mechanism of cation solvation by DOSO followed by ion-pair association with perchlorate. The composition of the extractable uranium(VI)-DOSO-perchlorate complex is most certainly analogous to those of TBP and TOPO which were described in an earlier section. The exceptionally strong extraction of gold(III) and palladium(II) is fairly convincing evidence for the existence of metal-sulfur coordination in their complexes.

A number of other metals not included in Figure 19 were chromatographed with 1 M perchloric acid only. No interaction was evident and so they were not studied further. The hydrolysis and/or polymerization of a few metals, titanium(IV), zirconium(IV), hafnium(IV), tin(IV), and antimony(V) prevented the study of their extraction from dilute perchloric acid.

The very limited extraction of metals from perchloric acid by DOSO suggests a very useful separation. At 0.01 - 6.0 M perchloric acid, uranium(VI), palladium(II) and gold(III) can be separated from all other metals studied. The uranium(VI)-DOSO-perchloric acid system has been examined in detail and will be discussed in a future section.

#### Miscellaneous systems

A number of metals were chromatographed on paper impregnated with di-n-octyl sulfone to determine if, as assumed, sulfones possess little coordinating ability. The metals studied were chosen on the basis of being the ones most likely to be extracted by a neutral donor from the particular acids used as eluents. The extraction of metals by di-n-octyl sulfone, as shown in Table 8, is negligible compared to the blanks. This indicates that the presence of small amounts of sulfone impurities should not effect the solvent extraction behavior of sulfoxides.

#### Solvent Extraction and Reversed-Phase Column Chromatography

##### Miscellaneous systems

Di-n-butyl sulfoxide/methyl isobutyl ketone - nitric acid/uranium(VI)

DBSO is the highest molecular weight aliphatic sulfoxide that is



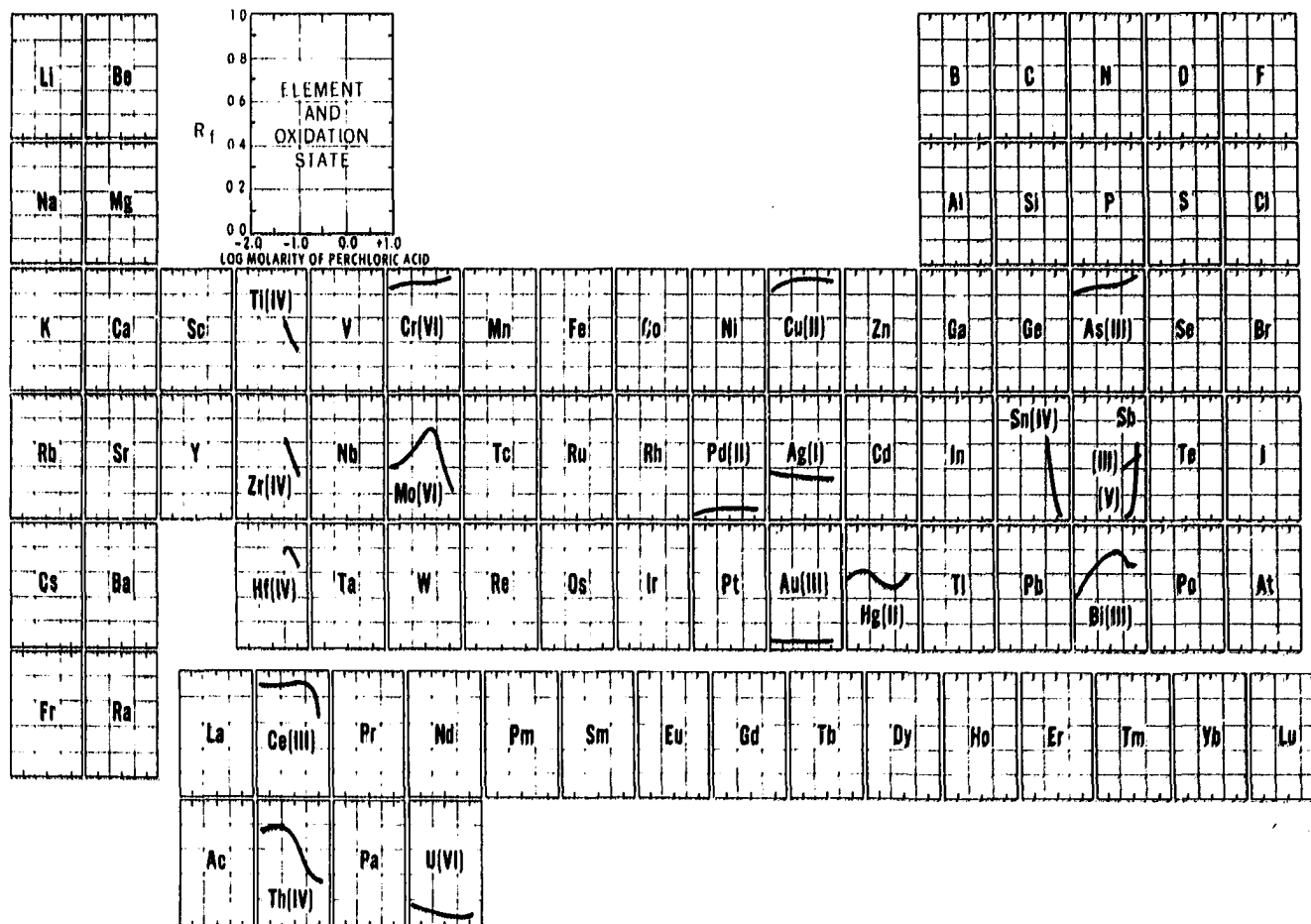


Figure 19. The chromatographic behavior of metal ions on paper impregnated with di-n-octyl sulfoxide eluted with perchloric acid

Table 8. The chromatographic behavior of metals on paper impregnated with di-n-octyl sulfone and eluted with 8 M nitric or hydrochloric acid

Metal	8 M nitric acid		8 M hydrochloric acid	
	R <sub>f</sub> impregnated	R <sub>f</sub> blank	R <sub>f</sub> impregnated	R <sub>f</sub> blank
Ti(IV)	0.92	0.91	0.78	0.75
Zr(IV)	0.83	0.92	0.77	0.81
Hf(IV)	0.96	0.96	0.77	0.86
Th(IV)	0.94	0.92	0.81	0.81
U(VI)	0.88	0.87	0.78	0.73
Pd(II)	0.74	0.70	0.63	0.70
Au(III)	0.70	0.66	0.61	0.53
Hg(II)	0.86	0.86	0.77	0.76
Sb(V)	0.73	0.66	0.73	0.43
Sn(IV)	0.90	0.86		
Fe(III)			0.82	0.75
Ga(III)			0.73	0.65
Zn(II)			0.82	0.80
Co(II)			0.86	0.85
Pt(IV)			0.64	0.70
Cd(II)			0.35	0.84

commercially available. It was briefly studied as a reagent for extracting uranium(VI) from nitric acid. Twenty milliliters of a 6 M nitric acid solution, containing 0.824 mmoles of uranyl nitrate, was extracted with an equal volume of 1 : 1 DBSO in methyl isobutyl ketone. The aqueous phase, after removing the nitric acid, was analyzed for uranium by the method of Sill and Peterson (60).

Four extractions were performed giving an average distribution ratio of 14.8 which corresponds to 93.2% extraction. Owing to the low extraction of uranium(VI) and to the high solubility of DBSO in aqueous acid systems, this reagent was not studied further.

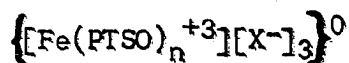
p-Tolyl sulfoxide/1,2 dichloroethane - nitric acid, perchloric acid/iron(III), ruthenium(III) In the discussion of the results of the paper chromatography survey, it was observed that iron(III) and ruthenium(III) were extracted from nitric acid by PTSO (Figure 16). To confirm this unexpected and unusual behavior, some brief solvent extraction experiments were performed.

A 1.0 M solution of PTSO in 1,2 dichloroethane was used to extract iron(III) and ruthenium(III) from 10 M nitric acid. The extraction of both metals resulted in the formation of an intense, red-orange color in the organic phase. The extent of extraction of ruthenium(III) was estimated to be greater than 90% on the basis of the decrease in the intensity of the color of the aqueous phase. A distribution ratio was calculated for iron(III) from an analysis of the aqueous phase before and after extraction. Iron(III) was found to be 98.6% extracted which corresponds to a distribution ratio of 63.9. It was observed that the iron could be recovered by back-extracting the organic phase with dilute nitric acid or with water.

An extraction of iron(III) from perchloric acid was also performed to determine if the nitrate ion plays a unique role in the extraction. A 0.01 M solution of iron(III) perchlorate in 1 M perchloric acid was extracted with 1.0 M PTSO in 1,2 dichloroethane, resulting in a highly colored organic phase which was indistinguishable from that obtained with nitric acid. The iron(III) in the aqueous phase was found to be 98.1% extracted.

The above data indicate that the extractable species in each case

is probably



where  $\text{X}^-$  is nitrate or perchlorate. That perchlorate is a more easily extractable counter ion than nitrate accounts for the strong extraction from a lower acid concentration. The change in the color of iron(III) from a very pale yellow in the aqueous phase to an intense red-orange in the organic phase indicates that the bonding in the iron(III)-PTSO complex may be other than simple solvation by the sulfinyl oxygen. Owing to the very similar ligand strengths of the sulfoxide group and water, the color of metals and metal complexes solvated by sulfoxides is nearly always the same as that of the corresponding aquo derivative (26).

bis(n-Octylsulfinyl)ethane/1,2 dichloroethane - perchloric acid/uranium(VI) An attempt was made to determine the combining ratio of BOSE with uranium(VI) extracted from perchloric acid. Solutions containing 0.01 mmoles of uranyl perchlorate in 1 M perchlorate were extracted with solutions which contained varying concentrations of BOSE in 1,2 dichloroethane. A plot of log distribution ratio as a function of log molarity BOSE is presented in Figure 20. The slope is higher than that expected for a bidentate ligand (two), but lower than that expected for a monodentate ligand (four). That this sample of BOSE was known to contain a sulfoxide-sulfone impurity may partially account for the high slope. Another factor may be that not all the BOSE molecules are coordinated in a bidentate manner. In any event, it is apparent that chelation is, for the most part, responsible for the extraction.

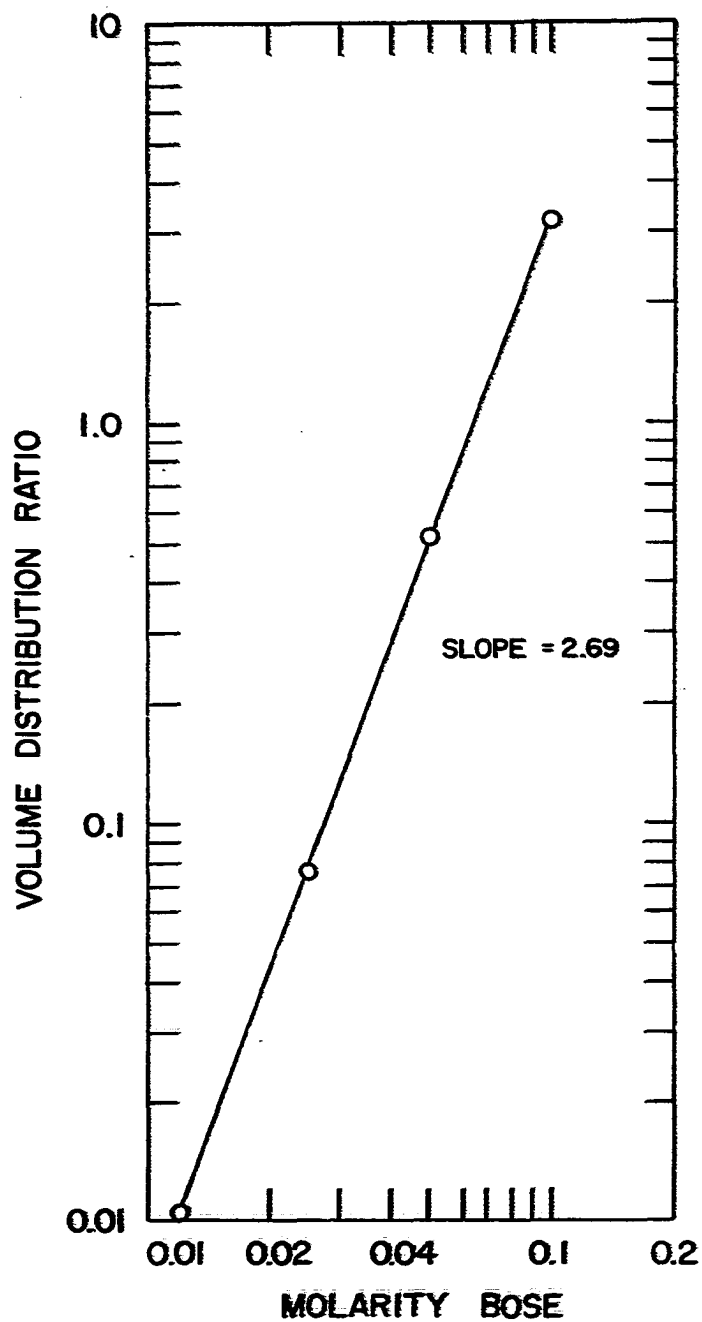


Figure 20. The distribution ratio of uranium(VI) extracted from 1 M perchloric acid as a function of the concentration of BOSE in the organic phase

The weakness of bidentate coordination in bis sulfoxides is illustrated by the data in Table 9 which compare the distribution ratios for uranium(VI) obtained with several extractants. The value for DOSO was determined by the author as will be discussed in a later section. The values for TOPO and MHDPO were taken from the work of O'Laughlin (35). The distribution ratio for 0.1 M MHDPO has been extrapolated from the value at 0.05 M.

Table 9. Distribution ratios for the extraction of uranium(VI) from 1 M perchloric acid by 0.1 M solutions of some neutral polar extractants

Extractant	Distribution ratio
DOSO	0.20
BOSE	3.10
TOPO	7.0
MHDPO	$1.6 \times 10^4$

It can be seen that the distribution ratio for uranium(VI) increases nearly four orders of magnitude in going from TOPO to MHDPO which clearly shows the advantage of bidentate coordination in bis phosphine oxides. However, the distribution ratio increases only 15 fold in going from DOSO to BOSE. This graphically illustrates the ineffectiveness of bidentate coordination in bis sulfoxides and supports the claim for steric hindrance in these compounds.

Di-n-octyl sulfoxide/1,2 dichloroethane - ammonium thiocyanate/  
zinc(II), cadmium(II), mercury(II) In the earlier discussion of the results of the paper chromatography survey, anomalous behavior was noted for zinc(II), cadmium(II), and mercury(II) on paper impregnated with DOSO and eluted with ammonium thiocyanate - 1 M perchloric acid (Figure 17). That zinc(II) and mercury(II) were seen to extract, whereas cadmium(II) was not, was considered worthy of further investigation. To confirm this behavior, 0.02 M solutions of zinc(II), cadmium(II), and mercury(II) chlorides in 0.50 M ammonium thiocyanate - 1 M perchloric acid were extracted with equal volumes of 0.5 M DOSO in 1,2 dichloroethane. Table 10 lists the results of the extractions. For purposes of comparison, the paper chromatography data have been included. There is fairly good correlation (except in the case of mercury(II)) between the distribution ratios obtained in the two systems.

Table 10. The extraction of metals from 0.5 M ammonium thiocyanate - 1 M perchloric acid into DOSO in 1,2 dichloroethane and on paper

Metal	Solvent extraction		Paper chromatography	
	% extraction	Distribution ratio	Distribution ratio $(\frac{1}{R_f} - 1)$	$R_f$
Zn(II)	98.2	56.	49.	0.02
Cd(II)	2.02	0.021	0.08	0.93
Hg(II)	47.3	0.90	9.0	0.10

The solvent extraction data indicate that cadmium(II) and mercury(II) can be easily separated from zinc(II) using reversed-phase column chromatography.

Di-n-octyl sulfoxide/cyclohexane - hydrochloric acid/zinc(II), zirconium(IV), hafnium(IV) A study was made of the extraction of zinc(II), zirconium(IV), and hafnium(IV) from hydrochloric acid solutions into DOSO dissolved in cyclohexane. Solutions of varying concentration of hydrochloric acid which contained 0.01 M metal were extracted with 0.1 M DOSO in cyclohexane. The results of the extractions are presented in Figure 21.

The extraction of curves of zirconium(IV) and hafnium(IV) show a very rapid increase with increasing hydrochloric acid molarity, while that of zinc(II) shows but a gradual increase. In the extractions of zinc(II), normal, two-phase systems were encountered. The extractions of the other two metals, however, were characterized by the formation of a third, solid phase. In such cases, the organic phase was composed of a white, finely-divided solid (which contained all the metal) suspended in cyclohexane. It is supposed that the extracted complex is insoluble in a medium of low dielectric constant such as cyclohexane. To confirm this supposition, solutions of 0.01 M zirconium(IV) in 8 M hydrochloric acid were extracted with 0.1 M solutions of DOSO in the following diluents: benzene, carbon tetrachloride, methyl isobutyl ketone, diethyl ether, ethyl acetate 2-ethylhexanol, trichloroethylene, *n*-butyronitrile and chloroform. Solid phases formed in all extractions except those in which butyronitrile and chloroform were used as diluents. Nearly quantitative extraction of zirconium(IV) was obtained in both cases which confirms that these two diluents are effective in solvating the extracted complex. The extraction of zirconium(IV) and hafnium(IV) by DOSO in chloroform was studied further and will be discussed in a later section.



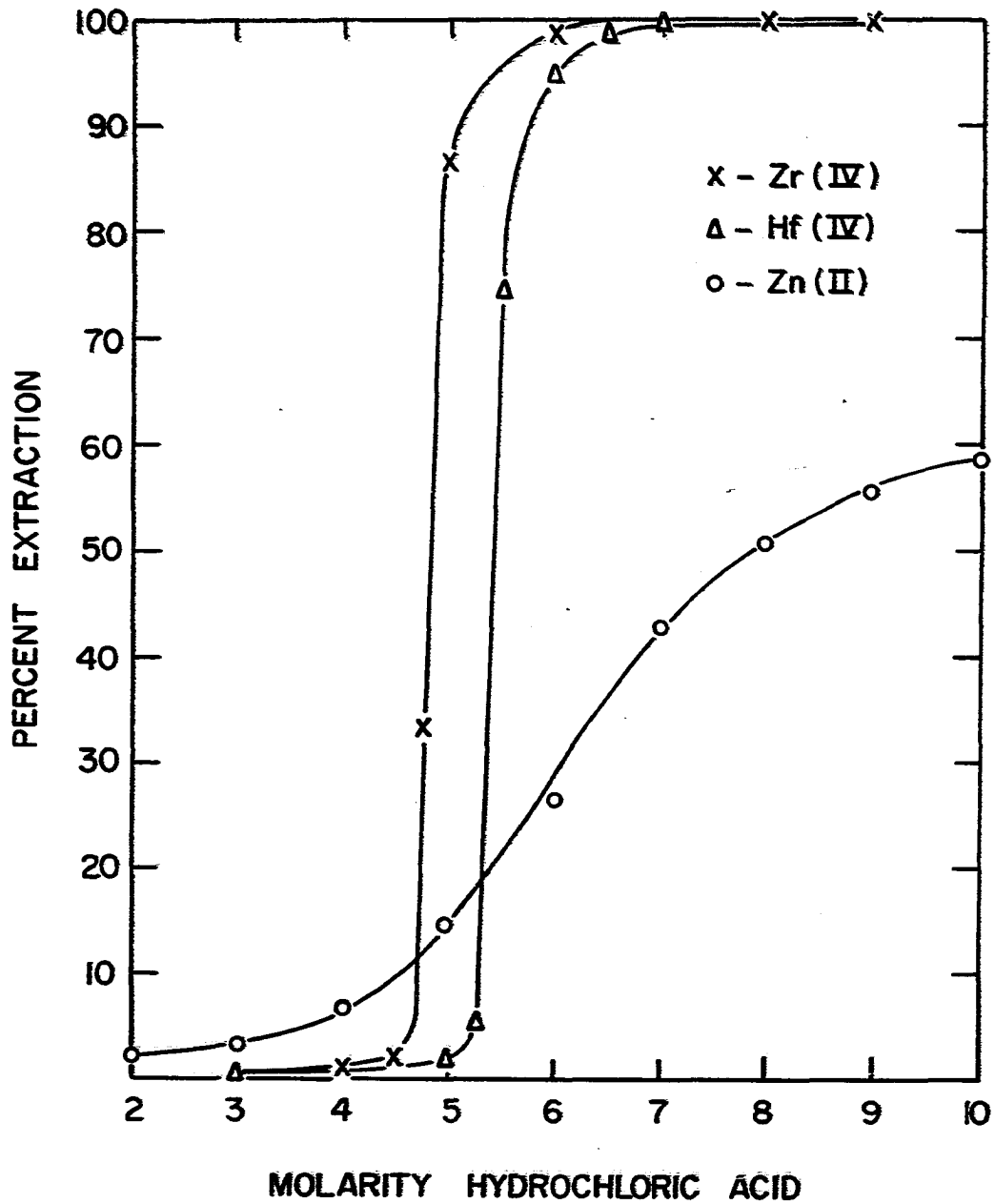


Figure 21. The percents of extraction of zinc(II), zirconium(IV), and hafnium(IV) into 0.1 M DOSO in cyclohexane as a function of hydrochloric acid concentration

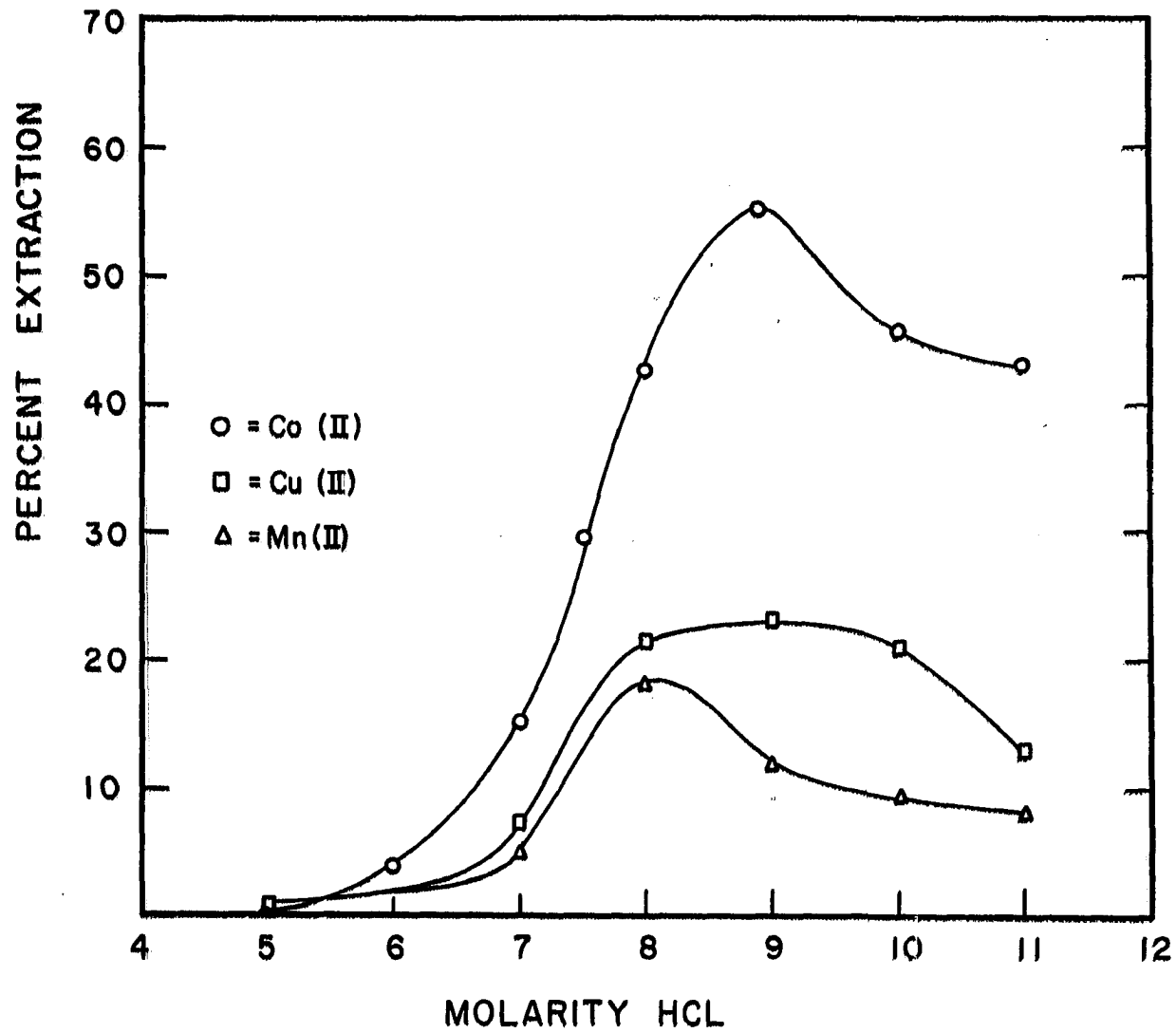
The formation of a third phase makes extractions by DOSO in cyclohexane undesirable for an analytical separation of zirconium(IV) and hafnium(IV). However, the unusually large difference in the magnitude of extraction of these two metals from 5 M hydrochloric acid might be of value in large scale separations.

Di-n-octyl sulfoxide/carbon tetrachloride - hydrochloric acid/  
manganese(II), cobalt(II), copper(II) A study was made of the extraction of manganese(II), cobalt(II), and copper(II) from hydrochloric acid into DOSO in carbon tetrachloride. Solutions of varying concentration of hydrochloric acid which contained 0.01 M metal were extracted with 0.2 M DOSO in carbon tetrachloride. The results of these extractions are presented in Figure 22. Table II compares the maximum distribution ratio of the three metals as obtained by solvent extraction and by paper chromatography and also compares the hydrochloric acid molarity at which maximum extraction occurs (M max).

Table II. The extraction of metals from hydrochloric acid solution into DOSO in carbon tetrachloride and on paper

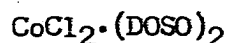
Metal	Solvent extraction		Paper chromatography	
	Distribution ratio	<u>M</u> max	Distribution ratio ( $\frac{1-R_f}{R_f}$ )	<u>M</u> max
Mn(II)	0.22	8.0	0.25	7.0
Co(II)	1.22	9.0	1.50	8.5
Cu(II)	0.30	9.0	0.67	9.0

Figure 22. The percents of extraction of manganese(II), cobalt(II), and copper(II) into 0.2 M DOSO in carbon tetrachloride as a function of hydrochloric acid concentration



These comparisons illustrate the value of paper chromatography data in predicting solvent extraction behavior.

Two experiments were performed to determine the composition of the complex formed in the extraction of cobalt(II) from hydrochloric acid into DOSO in carbon tetrachloride. In the first experiment, 0.01 M solutions of cobalt(II) in 9 M hydrochloric acid were extracted with carbon tetrachloride solutions of varying DOSO concentration. A plot of log distribution ratio as a function of log molarity DOSO is presented in Figure 23. The slope indicates that the ratio of cobalt(II) to DOSO in the complex is 1 : 2. In the second experiment, the organic phase from one of the above described extractions was evaporated to dryness and dissolved in acetone. Water was added to hydrolyze the complex and the amounts of cobalt(II) and chloride in the solution were determined by titration. The ratio of cobalt(II) to chloride in solution was found to be 1 : 2 and since hydrochloric acid is not extracted under these conditions (46), this is also the ratio in the complex. Therefore, the composition of the extractable complex is:



From a knowledge of the coordination chemistry of cobalt(II) and the solvent extraction properties of sulfoxides, this is certainly the type of complex one would expect.

Di-n-octyl sulfoxide/chloroform - hydrochloric acid/group (IV) metals

From the paper chromatography data (Figure 7), it appears that a separation of thorium(IV) from titanium(IV), zirconium(IV), and hafnium(IV) (and also a separation of zirconium(IV) from hafnium(IV))

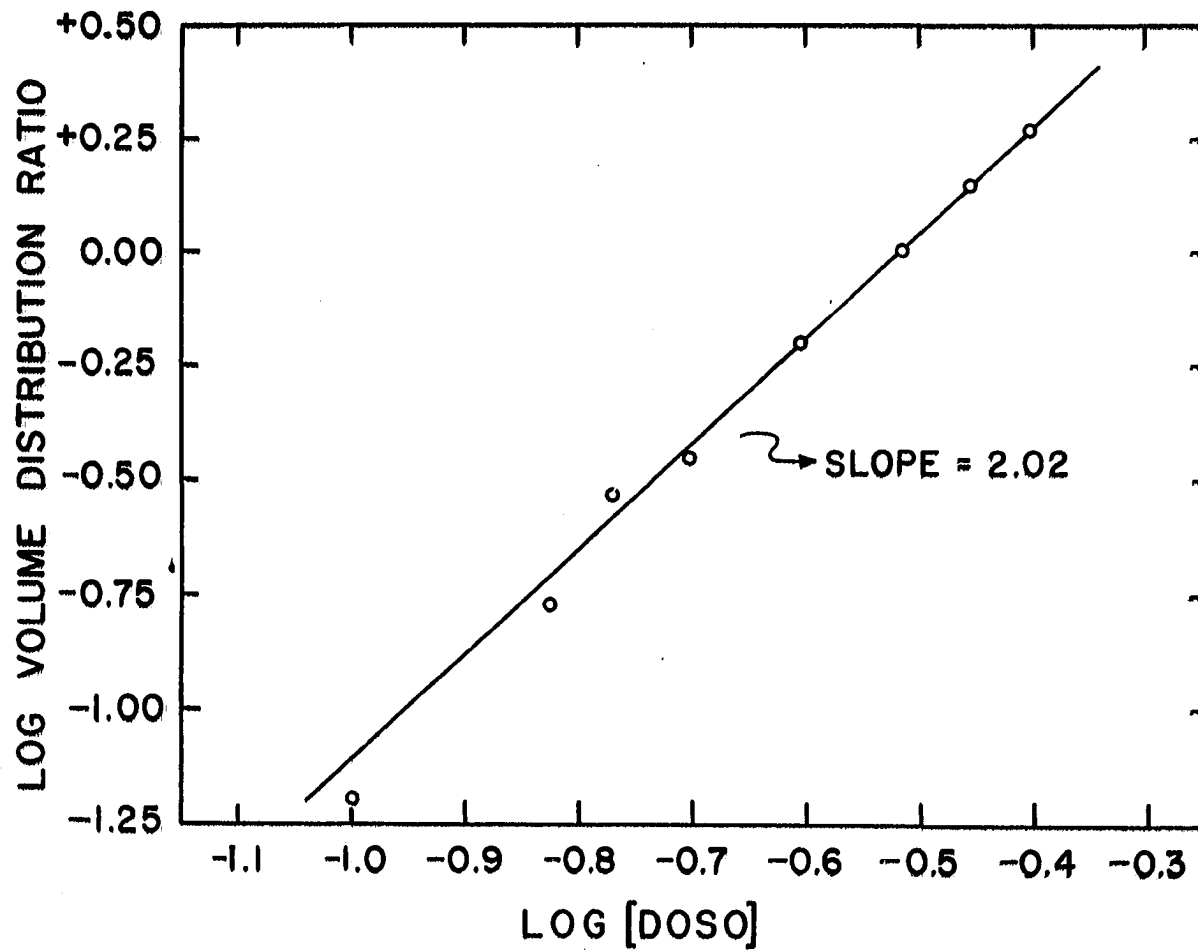


Figure 23. The distribution ratio of cobalt(II) extracted from 9 M hydrochloric acid as a function of the concentration of DOSO in the organic phase

might be possible in a DOSO-hydrochloric acid system. As just described, the extraction of zirconium(IV) and hafnium(IV) was studied briefly using cyclohexane as the diluent for DOSO. However, this study was abandoned, owing to the formation of metal complexes which were insoluble in the organic phase. In the same study it was found that quantitative extraction of zirconium(IV) could be obtained in a normal, two-phase system when chloroform was used as the diluent. It was decided, therefore, to study the extraction of all four metals from hydrochloric acid into DOSO dissolved in chloroform. The object of this study was to develop a system for the mutual separation of titanium(IV), zirconium(IV), hafnium(IV), and thorium(IV).

Fundamental studies Solutions of varying molarity of hydrochloric acid which contained 0.01 M titanium(IV), zirconium(IV), hafnium(IV) or thorium(IV) were extracted with 0.1 M DOSO in chloroform. The percents of extraction of these metals as a function of hydrochloric acid molarity are presented in Figure 24. Qualitative and quantitative differences are noted between these curves, those obtained from the paper chromatography work, and those obtained from solvent extraction studies using cyclohexane diluent. The extraction curve of titanium(IV) has been shifted to higher acid concentrations and sharply decreased in magnitude. The moderate extraction of thorium(IV) on DOSO impregnated paper is virtually non-existent in this system\*. The extraction of

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\*The work of Guar and Mohanty (48), shows that the extraction of thorium(IV) from hydrochloric acid into 0.1 M di-n-pentyl sulfoxide dissolved in carbon tetrachloride passes through a maximum at 8 M hydrochloric acid. Similar behavior for thorium(IV) was observed in the paper chromatography survey.

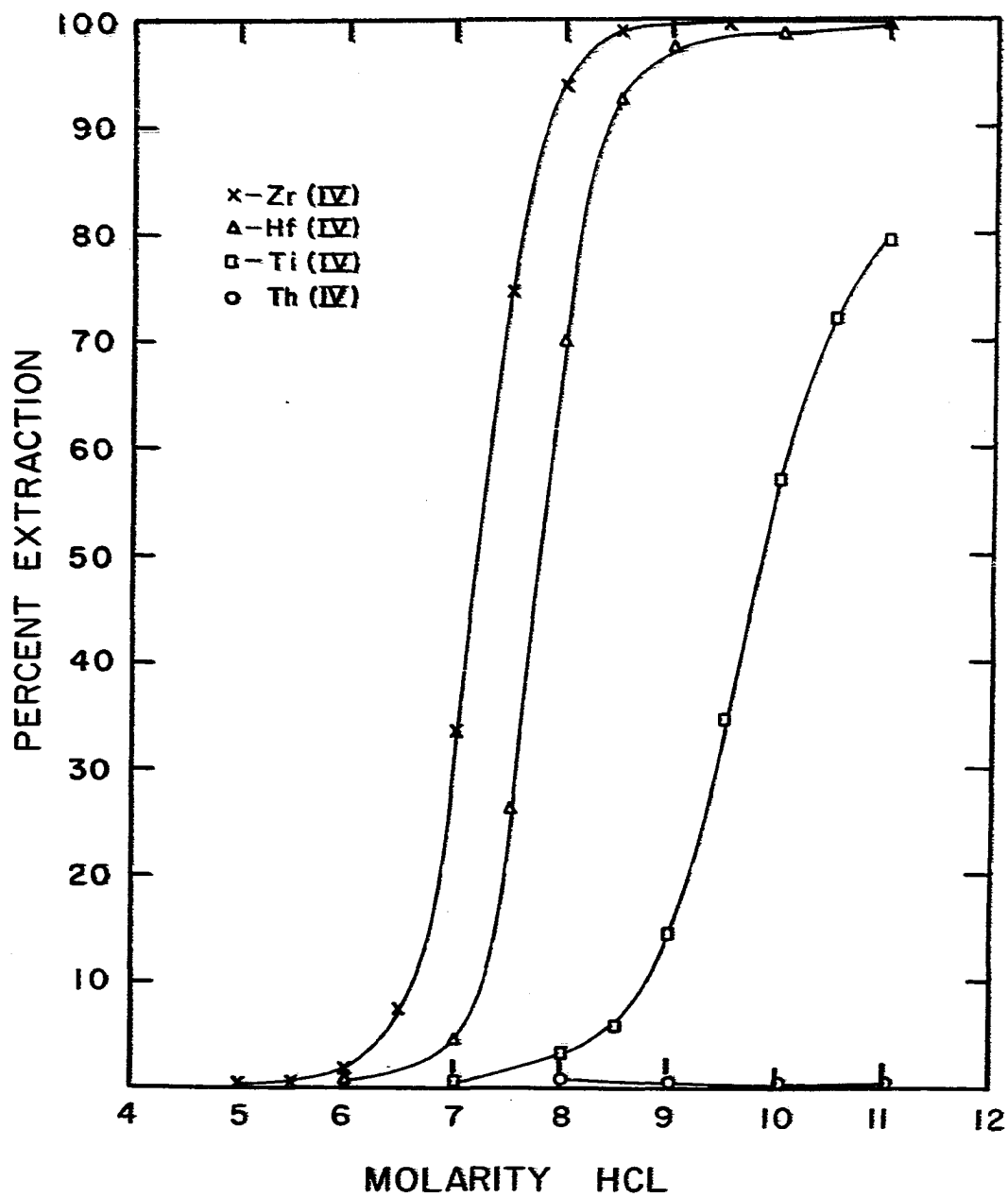


Figure 24. The percents of extraction of titanium(IV), zirconium(IV), hafnium(IV), and thorium(IV) into 0.1 M DOSO in chloroform as a function of hydrochloric acid concentration



zirconium(IV) and hafnium(IV), although still very high, has also been shifted to higher acid concentrations. All of these effects are apparently due to the use of chloroform as the diluent. As pointed out in an earlier section, strong hydrogen bonding between the diluent and the reagent can weaken the interaction between the reagent and the metal. Extensive hydrogen bonding between sulfoxides and chloroform has been observed (13) indicating that this phenomenon is responsible for the altered extraction behavior.

The data in Figure 24 indicate that in 8-11 M hydrochloric acid, zirconium(IV) and hafnium(IV) can be easily separated from thorium(IV) by reversed-phase column chromatography, or by batch extraction. The intermediate extraction of titanium(IV) will prevent a separation of this metal from either zirconium(IV) or thorium(IV) by batch extraction. However, it was determined that the addition of a drop of 30% hydrogen peroxide to the aqueous phase completely suppressed the extraction of titanium(IV), apparently owing to the formation of an unextractable, peroxy-complex. The extractions of zirconium(IV) and hafnium(IV) were not effected by the hydrogen peroxide, thus, making possible a batch extraction separation of these metals from titanium(IV). In Figure 25, the distribution ratios of titanium(IV), zirconium(IV), and hafnium(IV) are plotted as a function of hydrochloric acid molarity. From this presentation of the data, it appears that a reversed-phase column separation of zirconium(IV) and hafnium(IV) from titanium(IV) should be feasible using 9-11 M hydrochloric acid as the eluent. The difference in the extraction behavior of zirconium(IV) and hafnium(IV) ( $\alpha = 10$ ) indicates that a separation of these two metals may be possible. In 8 M

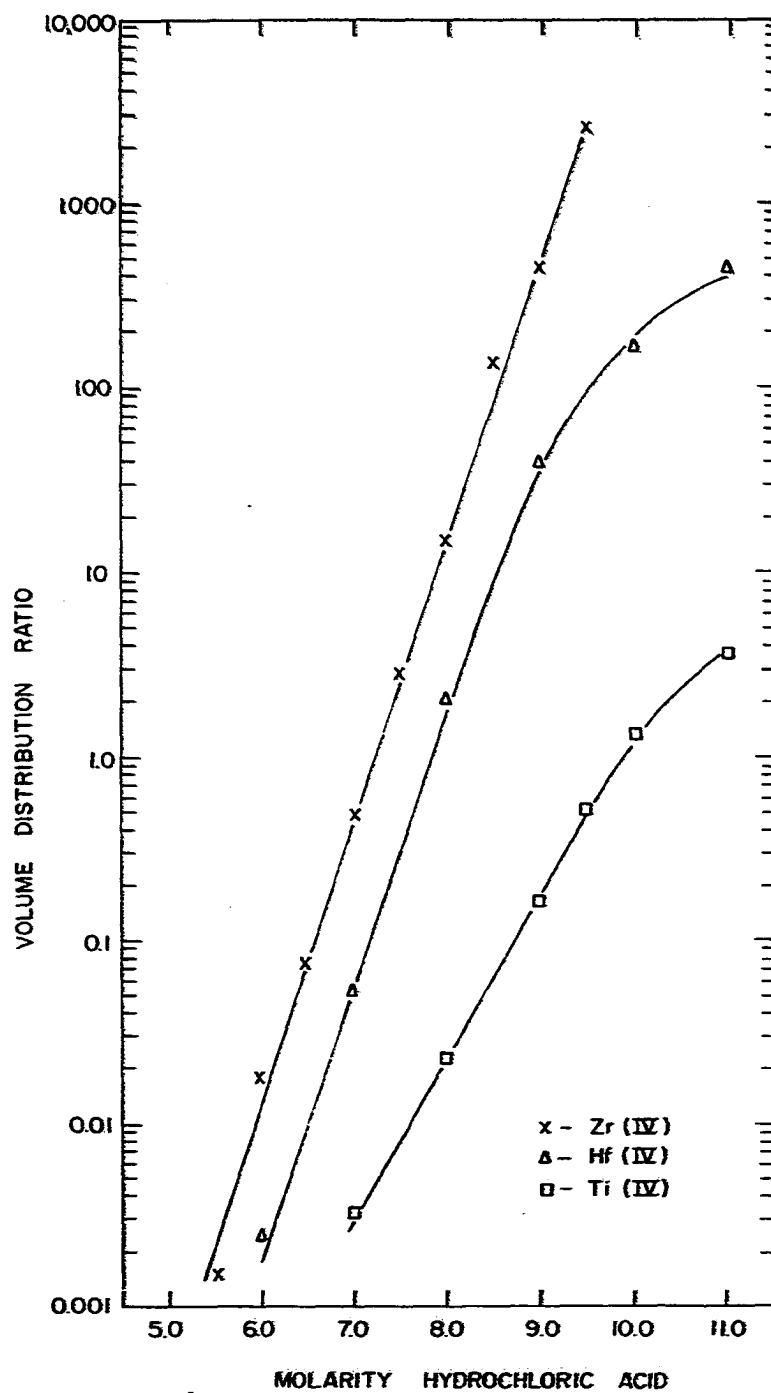


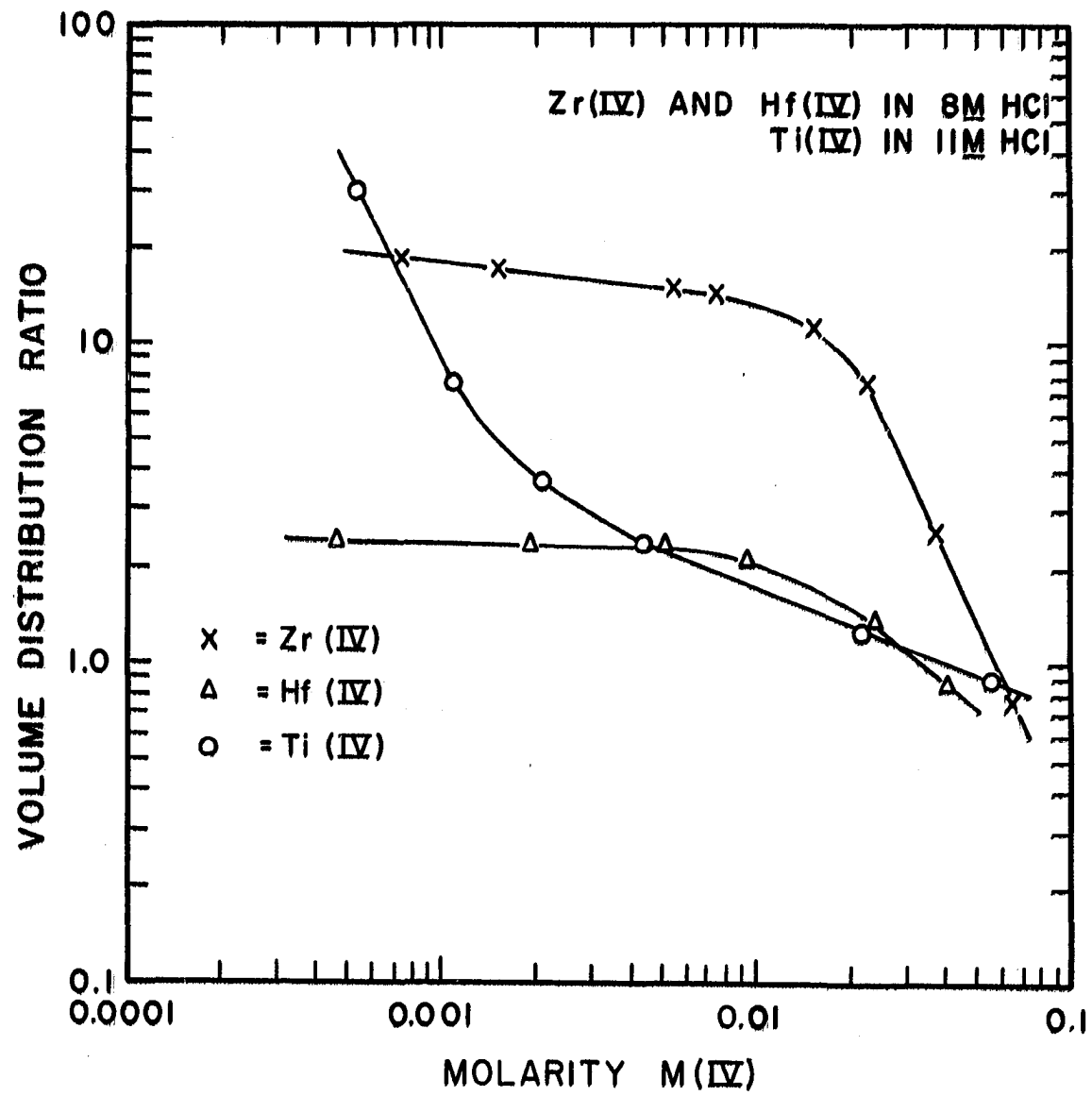
Figure 25. The distribution ratios of titanium(IV), zirconium(IV) and hafnium(IV) extracted into 0.1 M DOSO in chloroform as a function of hydrochloric acid concentration

hydrochloric acid, the distribution ratios are of the proper magnitude (zirconium(IV) = 15.0, hafnium(IV) = 1.60) for a reversed-phase column separation.

Before proceeding with the separation work, a study was made of the effect of metal "loading" upon the distribution ratios of titanium(IV), zirconium(IV), and hafnium(IV). Solutions of varying molarity of metal - zirconium(IV) and hafnium(IV) in 8 M hydrochloric acid, titanium(IV) in 11 M hydrochloric acid - were extracted with 0.1 M DOSO in chloroform. The results of this study are presented in Figure 26. These data indicate that, for column separation work, fairly low concentrations of metals ( $\leq 0.01$  M) must be used in order to prevent lowering of the distribution ratios. This is particularly true for the proposed separation of zirconium(IV) and hafnium(IV) where the separation factor is already quite small.

Analytical separations      Using the technique of liquid-liquid batch extraction, quantitative separations of hafnium(IV) from thorium(IV), and zirconium(IV) from titanium(IV) and thorium(IV) were performed. It was first determined that the zirconium(IV) or hafnium(IV) extracted from 10 M hydrochloric acid into 0.1 M DOSO in chloroform could be quantitatively back-extracted by solutions of 5 M hydrochloric acid. Synthetic, binary mixtures, consisting of solutions of 0.01 M metal in 10.5 M hydrochloric acid, were then extracted with 0.1 M DOSO in chloroform. Aliquots of the aqueous phases were analyzed for the metal not extracted, i.e., thorium(IV) or, when hydrogen peroxide was present, titanium(IV). Aliquots of the organic phases were back-extracted with

Figure 26. The distribution ratios of zirconium(IV) and hafnium(IV) in 8 M hydrochloric acid and titanium(IV) in 11 M hydrochloric acid extracted into 0.1 M DOSO in chloroform as a function of metal concentration originally present in the aqueous phase



5 M hydrochloric acid and the aqueous phases were analyzed for zirconium (IV) or hafnium(IV). Table 12 summarizes the results of these extractions.

Table 12. The liquid-liquid batch extraction separations of group (IV) metals

Experiment number	Metal	Amount added (mmoles)	Amount found (mmoles)	% Recovery
1	Zr(IV)	0.136	0.136	100.0
	Th(IV)	0.140	0.139	99.4
2	Hf(IV)	0.125	0.123	98.7
	Th(IV)	0.140	0.140	100.0
3	Zr(IV)	0.136	0.137	100.7
	Ti(IV)	0.173	0.165	95.4
4*	Zr(IV)	0.136	0.134	98.6
	Ti(IV)	0.173	0.173	100.0

\*Separation performed in 9.5 M hydrochloric acid.

Liquid-liquid batch extraction was also used to demonstrate the utility of the DOSO-hydrochloric acid system for purifying hafnium salts. A sample of hafnyl chloride, known to contain 2.7% zirconium, was used to prepare three solutions of 0.05 M hafnium(IV) in 7.5 M hydrochloric acid. These solutions were then extracted a varying number of times with 0.1 M DOSO in chloroform. After the required number of extractions, the metals in the aqueous phases were precipitated as the hydrous oxides and ignited to the oxides which were then analyzed by emission spectroscopy. Table 13 summarizes the results of these extractions.

A number of quantitative separations of thorium(IV), zirconium(IV),

Table 13. The removal of zirconium(IV) from hafnium chloride by batch extraction

Solution number	Number of extractions performed	Amount of zirconium(IV) remaining	
		per cent	parts per million
1	0	2.7	27,000
2	1	0.5	5,000
3	2	0.18	1,000
4	3	<0.02	< 200

and titanium(IV) were performed using reversed-phase column chromatography. A 30x1.2 cm. column, containing 1.0 M DOSO<sup>2</sup> in chloroform sorbed on 60-80 mesh Tee-Six powder, was used for all the separations. The column was first equilibrated with 20 ml. of 9 M hydrochloric acid and the metals were added as 0.01 M solutions also in 9 M hydrochloric acid. Thorium(IV) was first eluted with 60 ml. of the 9 M hydrochloric acid. The eluent was then changed to 8 M hydrochloric acid and titanium(IV) was eluted in the 60-115 ml. fraction. Next, the column was eluted with 6 M hydrochloric acid and zirconium(IV) was removed in the 115-170 ml. fraction. Finally, owing to the deterioration of the stationary phase after extended contact with strong hydrochloric acid, the column was eluted with distilled water.

A typical elution curve for a mixture of titanium(IV), zirconium(IV) and thorium(IV) is shown in Figure 27. Table 14 summarizes the results

\*It was necessary to use this higher concentration of DOSO owing to the difficulty in retaining titanium(IV) on columns containing 0.1 M DOSO.

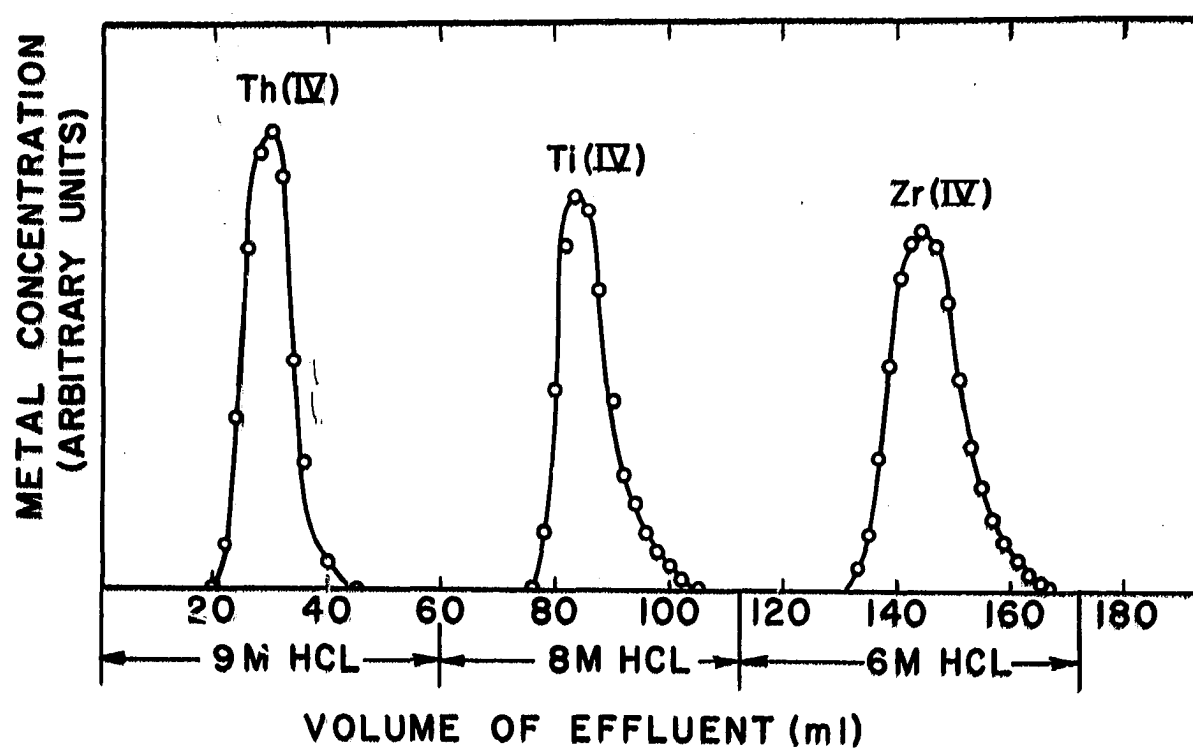


Figure 27. Elution curve for the separation of a mixture of thorium(IV), titanium(IV), and zirconium(IV) on a reversed-phase column employing 1.0 M DOSO in chloroform as the stationary phase



Table 14. Separations of group (IV) metals by reversed-phase, column chromatography

Experiment number	Metal	mmoles added	mmoles found	Percent recovery
1	Th(IV)	0.0561	0.0560	99.8
	Zr(IV)	0.0356	0.0357	100.3
2	Th(IV)	0.0561	0.560	99.8
	Zr(IV)	0.0356	---	---
3	Th(IV)	0.0561	0.0560	99.8
	Zr(IV)	0.0356	0.0356	100.0
4	Th(IV)	0.0561	0.0561	100.0
	Zr(IV)	0.0356	0.0356	100.0
5	Th(IV)	0.0561	0.0560	99.8
	Zr(IV)	0.0356	0.0356	100.0
6	Th(IV)	0.0510	0.0509	99.7
	Zr(IV)	0.0547	0.0546	99.8
7	Th(IV)	0.255	0.253	99.2
	Zr(IV)	0.0574	0.0592	103.1
8	Th(IV)	0.0499	0.0499	100.0
	Ti(IV)	0.0562	0.0562	100.0
9	Th(IV)	0.0499	0.0498	99.8
	Ti(IV)	0.0562	---	---
10	Th(IV)	0.0499	0.0498	99.8
	Ti(IV)	0.0562	0.0562	100.0
11	Th(IV)	0.0499	0.0497	99.6
	Ti(IV)	0.0562	0.0560	99.7
12	Zr(IV)	0.0547	0.0545	99.6
	Ti(IV)	0.0494	0.0511	103.5
13	Zr(IV)	0.0274	0.0273	99.5
	Ti(IV)	0.247	0.244	98.8

Table 14 (Continued)

Metal	Average recovery (%)	Relative standard deviation (%)
Th(IV)	99.8	0.2
Zr(IV)	99.9*	0.3
Ti(IV)	99.6*	0.6

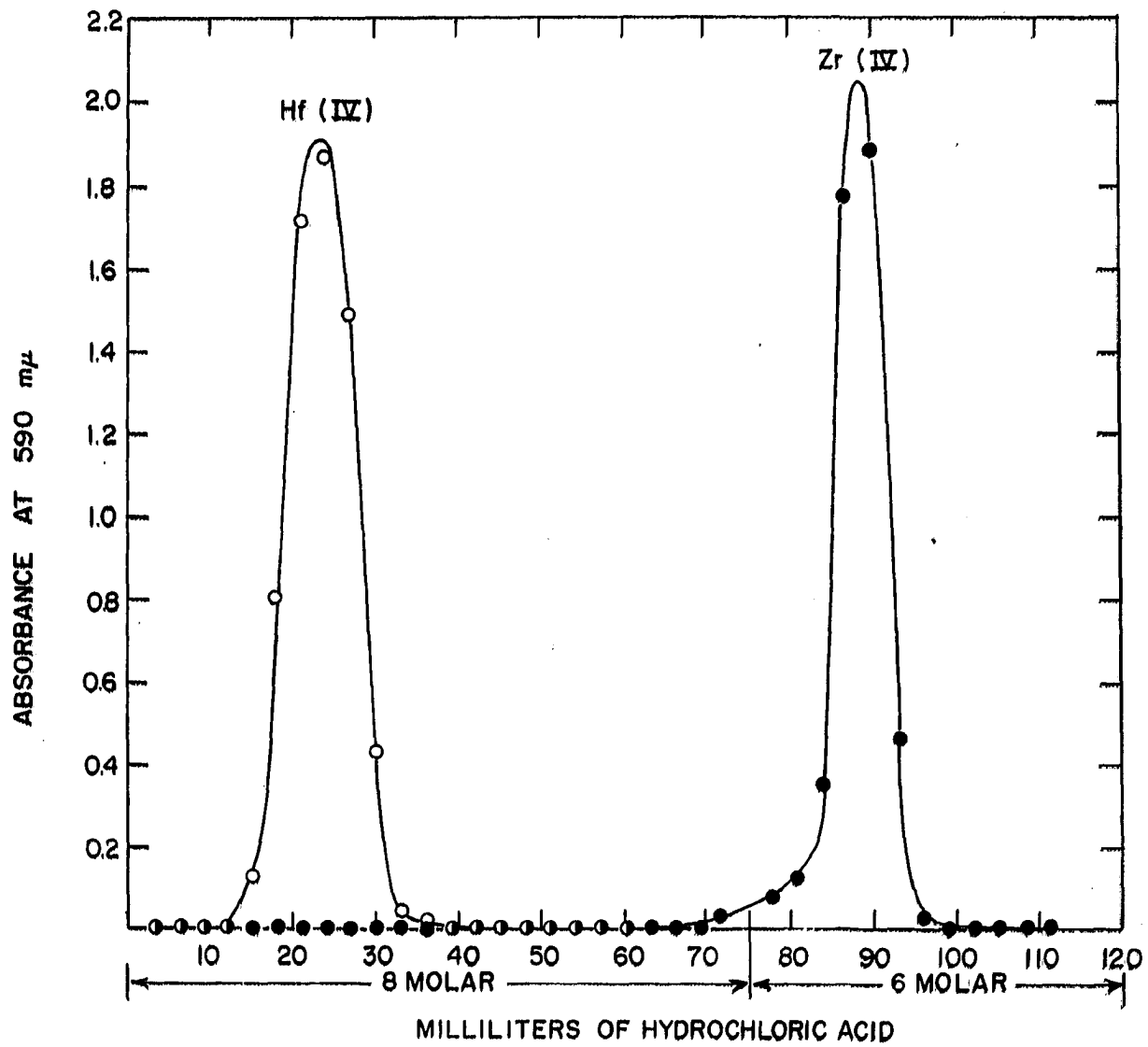
\*The zirconium(IV) result of experiment number 7 and the titanium(IV) result of experiment number 12 were rejected by the three sigma test.

of the column separations.

As previously noted, the data in Figures 25 and 26 indicate that a separation of zirconium(IV) from hafnium(IV) on a reversed-phase column should be possible when using 0.1 M DOSO in chloroform as the stationary phase and 8 M hydrochloric acid as the eluent. Several quantitative separations of zirconium(IV) from hafnium(IV) were, indeed, performed using this system. A 24x1.4 cm. column, which contained the stationary phase sorbed on 60-80 mesh XAD-2, was used for all separations. After the column had been equilibrated with 20 ml. of eluent, the sample was added as a 0.01 M solution of zirconium(IV) and hafnium(IV) in 8 M hydrochloric acid. The same concentration of acid was then generally used to elute both metals from the column.

Figure 28 shows the superimposed, individual curves obtained for the elution of 0.0238 mmoles of hafnium(IV) and 0.0334 mmoles of zirconium(IV) as determined by the absorbances of their Arsenazo I complexes. The eluent was changed to 6 M hydrochloric acid at 75 ml. so as to more rapidly elute the zirconium(IV). This accounts for the unusual shape of

Figure 28. Individual elution curves of zirconium(IV) and hafnium(IV) on a reversed-phase column containing 0.1 M DOSO in chloroform sorbed on 60-80 XAD-2



that elution curve. These curves indicate that the separation of a mixture of zirconium(IV) and hafnium(IV) is feasible using the present system.

A mixture of 0.0595 mmoles of hafnium(IV) and 0.0835 mmoles of zirconium(IV) was qualitatively separated as shown in Figure 29. The increased amounts of metals used in this separation have caused a somewhat premature breakthrough of zirconium(IV), but have not effected the elution behavior of hafnium(IV). Even at these higher loadings it appears that a quantitative separation should be possible.

Based on the elution curves in Figures 28 and 29, three quantitative separations of mixtures of zirconium(IV) and hafnium(IV) were performed. In each experiment, after sorption of the sample, the column was eluted with 8 M hydrochloric acid and the first 50 ml. of effluent was collected for the hafnium(IV) fraction. The eluent was then changed to 6 M hydrochloric acid and the next 30 ml. of effluent was collected for the zirconium(IV) fraction. The results of these separations are summarized in Table 15. In separation 1, the fractions were analyzed by EDTA titration. In separations 2 and 3, the zirconium(IV) and hafnium(IV) fractions (after their contents had been converted to the metal oxides) were analyzed for cross contamination by emission spectroscopy.

Separation number 1 appears to be quantitative but, since the analytical method used was non-specific, there could be cross contamination. However, this is unlikely in light of the very small amounts of cross contamination indicated for separation number 2. It is not until rather high metal loading is reached, as in separation number 3, that significant quantities of zirconium(IV) appear in the hafnium(IV) fraction and vice versa.

Figure 29. Elution curve for the separation of a mixture of equivalent amounts of zirconium(IV) and hafnium(IV)

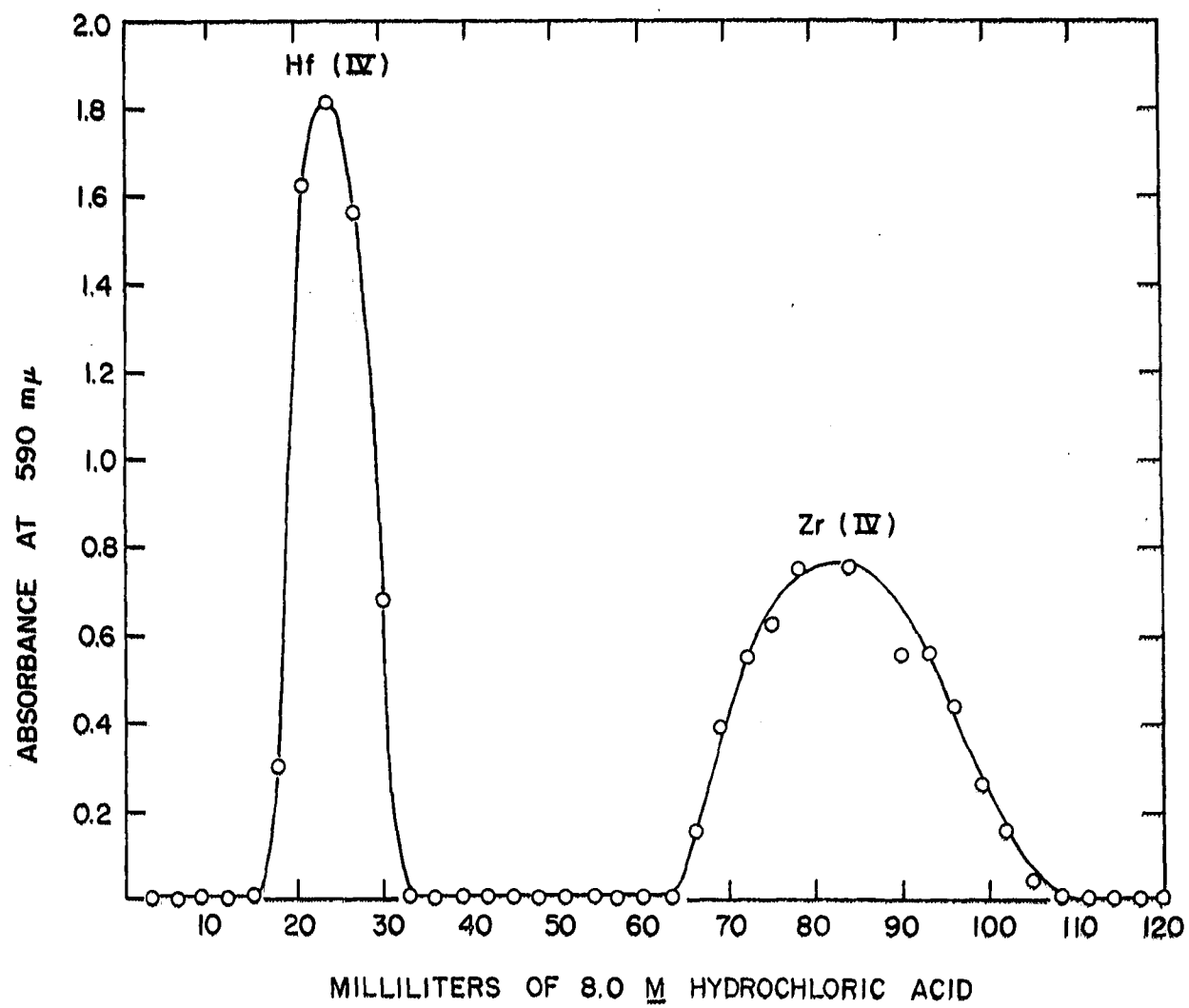


Table 15. Separations of zirconium(IV) from hafnium(IV) by reversed-phase column chromatography

Separation number	Metal	mmoles added	mmoles found	% Recovery
1	Hf(IV)	0.0357	0.0359	100.6
	Zr(IV)	0.0502	0.0502	100.0
2	Hf(IV)	0.0545	% Zr(IV) < 0.01	% Hf(IV) Major
	Zr(IV)	0.0835	Major	< 0.02
3	Hf(IV)	0.119	0.5	Major
	Zr(IV)	0.167	Major	0.1

A final experiment was performed in which a trace amount of hafnium (IV) was separated from a moderate amount of zirconium(IV). The sample used for this separation contained  $3.41 \times 10^{-6}$  mmoles of hafnium(IV) and possessed a  $\text{Hf}^{181}$  activity of 0.1 microcuries. Also present in the sample was  $3.34 \times 10^{-2}$  mmoles of zirconium(IV), thus giving a 5000 fold excess (by weight) of zirconium(IV) over hafnium(IV). The sample was sorbed on the column and eluted with 120 ml. of 8 M hydrochloric acid. The elution curve for the separation of this mixture is shown in Figure 30.

Although the separation of the two metals is complete, there is some tailing of hafnium(IV) beyond 50 ml. of effluent. In situations where larger amounts of zirconium(IV) are to be employed, this tailing could result in some overlap of the two elution peaks. Cross contamination is apparently absent in the separated mixture. This is indicated by the lack of absorbance in the interval of 21-33 ml. and by the lack of



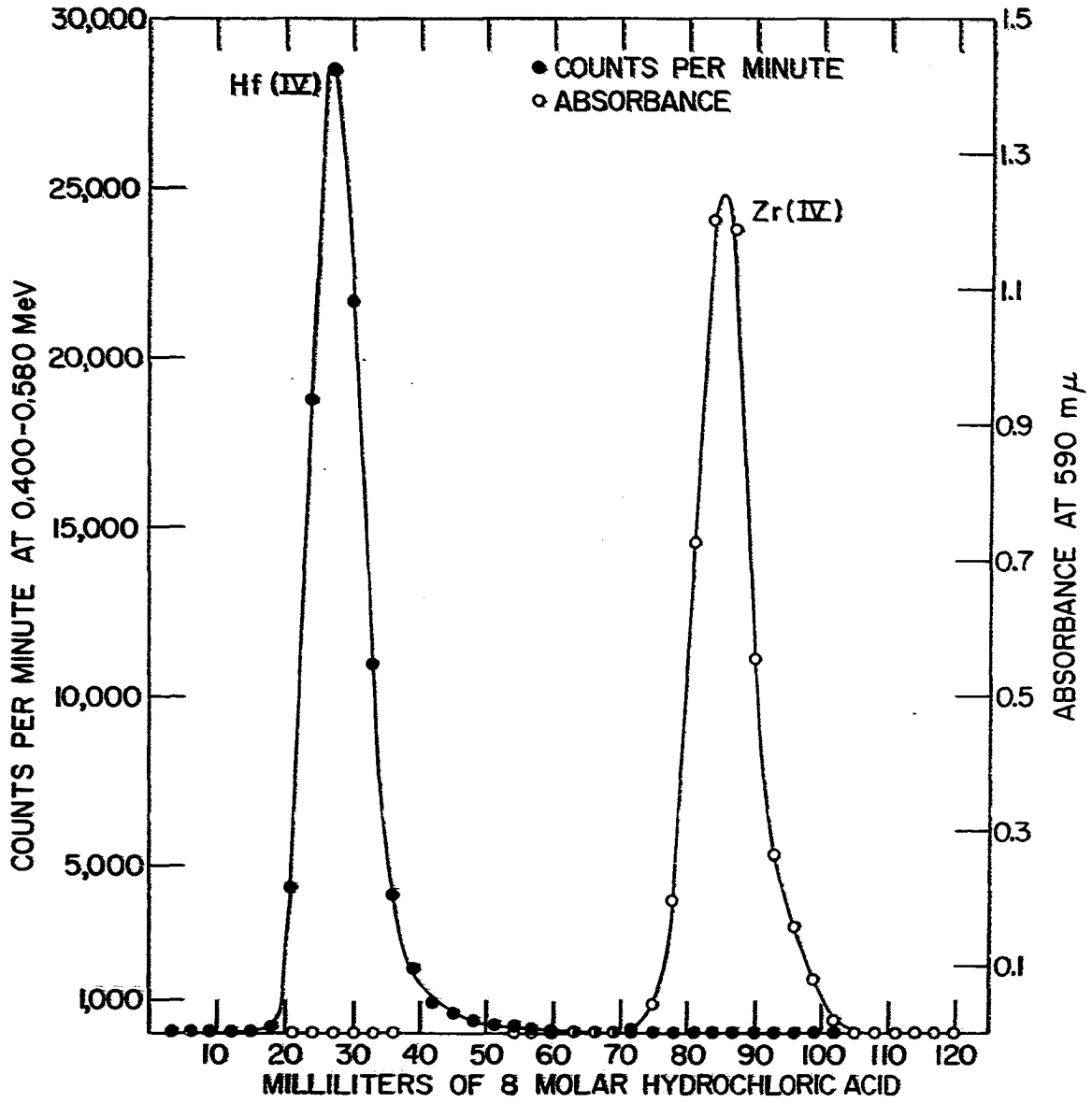


Figure 30. Elution curve for the separation of  $3.41 \times 10^{-6}$  mmoles of hafnium(IV) from  $3.34 \times 10^{-2}$  mmoles of zirconium(IV)

activity (above background) in the interval of 72-102 ml. The recovery of hafnium(IV) (as determined by the  $\text{Hf}^{181}$  activity added and recovered) was determined to be 99.2% for the 0-51 ml. fraction, 99.9% for the 0-60 ml. fraction, and 100.5% for the 0-72 ml. fraction.

Conclusions The system which has just been described for the separation of titanium(IV), zirconium(IV), hafnium(IV), and thorium(IV) could be of great utility to the analytical chemist. These four metals are becoming more frequently encountered in analyses and it is not unusual for them to occur together in the same sample. Owing to their similar chemical properties, a separation is quite often required in the course of an analysis, particularly when wet chemical methods are used. The present separation system is well adapted to this purpose.

The separation of these metals has been the subject of an exceptionally large number of publications. An exhaustive comparison of previously developed separation methods to the present one would be pointless. However, a few selected systems will be briefly described to render a perspective to the present research.

Cerrai and Testa (71) found that zirconium(IV) and thorium(IV) were readily separated on a reversed-phase column employing tri-*n*-octyl phosphine oxide (TOPO) as the stationary phase and 10 *M* hydrochloric acid as the eluent. These authors (72) also performed the same separation using tri-*n*-octyl amine (TNOA), a liquid anion exchanger, as the stationary phase. A paper by Fritz and Garraïda (73) describes the separation of thorium(IV) from zirconium(IV) (and a large number of

other metals) on an anion exchange column. Thorium(IV), one of the few metals to form a strong nitrate complex in 6 M nitric acid, is quite selectively retained.

Two excellent systems have been developed to separate both zirconium(IV) and titanium(IV) from thorium(IV). The first (74) uses 0.1 M hydrofluoric acid to rapidly elute the fluoride complexes of titanium(IV) and zirconium(IV) from a cation exchange column. The second (75) employs a reversed-phase column with TOPO as the stationary phase. Nitric acid and hydrochloric acid eluents are used to elute titanium(IV) and zirconium(IV), respectively, from thorium(IV).

Methods for the separation of zirconium(IV) and hafnium(IV) have been extensively studied. A mutual separation of these two metals and thorium(IV) has been described by Strelow and Bothma (76). The three metals were eluted sequentially from an anion exchange column by various concentrations of sulfuric acid. A number of additional ion exchange methods for the separation of zirconium(IV) and hafnium(IV) are described in Samuelson's book (77). Fritz and Frazee (78) describe a separation of the two metals on a reversed-phase column using methyl isobutyl ketone as the stationary phase. An ammonium thiocyanate-ammonium sulfate mixture is employed to selectively elute zirconium(IV). Using the previously described TNOA column (72), Cerrai and Testa were able also to separate zirconium(IV) and hafnium(IV) by eluting with 8 M hydrochloric acid.

Compared to these other methods, the DOSO-hydrochloric acid system is superior in some respects and comparable in others. The present

system is perhaps unique among similar solvent extraction systems in that it can accomplish a quantitative separation of zirconium(IV) from thorium(IV) by a single batch extraction. In this respect it even rivals the speed and selectivity of the ion exchange methods. The separation of zirconium(IV) from hafnium(IV) is comparable to that obtained using most other reversed-phase systems. Although the completeness of separation is superior in some ion exchange systems, the present system is favored by the rapidity of the separation and by the relatively small volume of eluent required.

The DOSO-hydrochloric acid system is perhaps of unique value in that it will permit a separation of all four metals on a single column using a single type of acid as the eluent. Even the separation of a four-component mixture, although not attempted in the present work, should be possible using this system.

Di-n-octyl sulfoxide/1,2 dichloroethane - perchloric acid/uranium(VI)

In the discussion of the paper chromatography data, the strong extraction of uranium(VI) from perchloric acid by DOSO was noted (Figure 19). The weak extraction of the fifty other metals studied (except gold(III) and palladium(II)) indicated that a nearly specific analytical separation of uranium(VI) might be possible in this system. It was decided, therefore, to study the extraction of uranium(VI) and other metals from perchloric acid solutions into DOSO dissolved in an organic diluent. From the results of this study, it was hoped that an extraction system could be developed which would permit the analytical

separation of uranium from most other metals.

Fundamental studies . An evaluation was first made of a number of organic solvents for use as diluents for DOSO. Solutions of 0.1 M DOSO were extracted with 0.01 M uranium(VI)\* in 1 M perchloric acid. A percent extraction was determined for each diluent and the number of phases resulting from the extraction was noted. The results of these extractions are summarized in Table 16.

The diluents in Table 16 are divided into two categories; two-phase systems and three-phase systems. In the three-phase systems, a viscous, yellow liquid or flaky, yellow solid (which apparently contained all the uranium) was formed between the aqueous phase and the diluent phase. It would seem that the uranium(VI)-DOSO-perchlorate complex cannot be solvated by these diluents of generally low dielectric constant. If the extractable species is an ion association complex (as was predicted in an earlier section) this is a reasonable supposition. It will be recalled that a similar phenomenon was observed during the extraction of zirconium(IV) from hydrochloric acid into DOSO dissolved in cyclohexane.

Although the three-phase systems are characterized by generally high extraction, they were considered to be unsuitable from an analytical viewpoint. The two-phase systems, unfortunately, were characterized by generally low extraction, probably owing to competitive solvation of

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\*All uranium(VI) solutions used in this work were prepared from uranyl perchlorate.

Table 16. The extraction of uranium(VI) from 1 M perchloric acid into 0.2 M DOSO dissolved in various diluents

Diluent	Extraction
Two-phase systems	
1. chlorobenzene	< 50%
2. chloroform	< 50%
3. <u>n</u> -hexanol	< 50%
4. <u>n</u> -octanol	< 50%
5. cyclohexanone	< 50%
6. trichloroethylene	50%
7. <u>n</u> -butanol	55%
8. 3-methyl-1-butanol	55%
9. 4-methyl-2-pentanone	65%
10. 5-methyl-2-hexanone	65%
11. <u>n</u> -butyronitrile	70%
12. 2-octanone	75%
13. 1,2 dichloroethane	75%
14. tri- <u>n</u> -butyl phosphate (0.1 <u>M</u> )	88.5%
15. <u>n</u> -propyl nitrate	92.5%
16. nitrobenzene	95%
Three-phase systems	
1. butyl acetate	70%
2. diethyl ether	88%
3. 2,6 dimethyl-4-heptanone	95%
4. benzene	95.0%
5. toluene	95.2%
6. carbon tetrachloride	96.8%
7. xylene	98.8%
8. di-isopropyl ether (0.1 <u>M</u> )	99.2%
9. cyclohexane (0.1 <u>M</u> )	99.5%
10. methyl laurate	99.8%

DOSO by the diluent. Of the diluents in this category, n-butyronitrile and 1,2 dichloroethane were selected for further study on the basis of their fairly adequate extraction and their clean, rapid phase separation properties.

A brief study was made of the effect of mixed diluents on the

extraction of uranium(VI). Solutions of 0.01 M uranium(VI) in 1 M perchloric acid were extracted with solutions of 0.1 M DOSO dissolved in mixtures of n-butyronitrile and cyclohexane. It was hoped that a mixture of these two solvents could be found that would give the high extraction that is characteristic of three-phase systems, yet still remain a two-phase system.

Figure 31 summarizes the results of these extractions. It can be seen that the amount of extraction indeed increases with increasing concentration of the non-polar diluent. However, the distribution ratios of the two-phase systems are still not sufficiently large for a quantitative extraction of uranium(VI) and so, the study of this system was discontinued.

The effect of the concentration of DOSO upon the extraction of uranium(VI) was the subject of the next experiment. Solutions of 0.01 M uranium(VI) in 1 M perchloric acid were extracted with 0.1 - 0.5 M DOSO in 1,2 dichloroethane\*. The results of this study are presented in Figure 32.

The slope of the line confirms that, as expected, the combining ratio of DOSO to uranium(VI) in perchlorate media is 4 : 1, indicating the formation of the species



in which DOSO ligands have completely filled the inner coordination sphere

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\*Owing to the limited solubility of DOSO in n-butyronitrile ( $\sim 0.2$  M), 1,2 dichloroethane was selected as the diluent for this and all future studies.

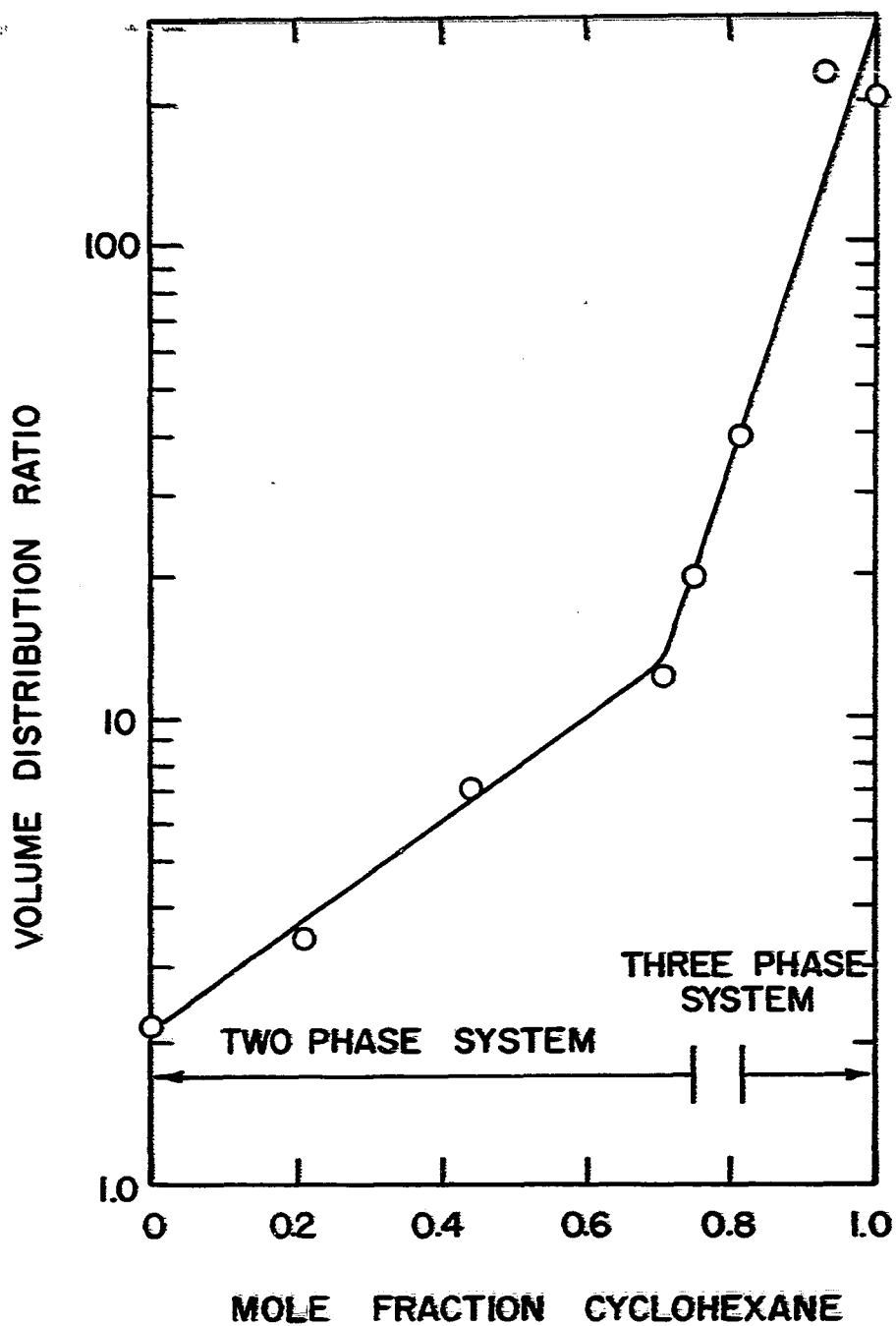
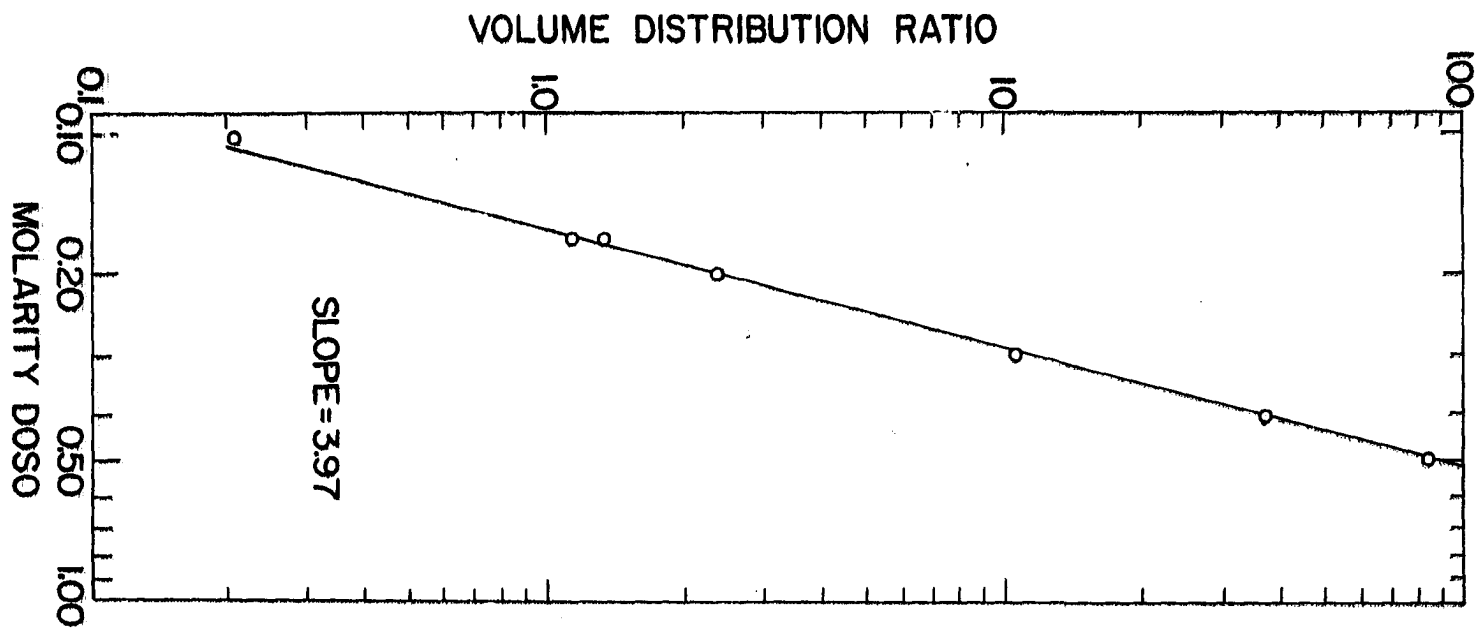


Figure 31. Extraction of uranium(VI) from 1 M perchloric acid into 0.1 M DOSO dissolved in mixtures of cyclohexane and butyronitrile



Figure 32. The distribution ratio of uranium(VI) extracted from 1 M perchloric acid as a function of the concentration of DOSO in the organic phase



of the uranyl ion. A practical ramification of the composition of the complex is that

$$D_v = k[\text{DOSO}]^4.$$

Thus, in going from 0.1 M to 0.5 M DOSO, the distribution ratio has increased nearly 500 fold. It was decided that the concentration of DOSO would be limited to 0.5 M for future extraction studies.

A few brief experiments were performed to determine how the uranium (VI), once extracted, could best be recovered from the organic phase. Back-extraction with dilute sulfuric acid solutions was found to be most satisfactory for this purpose. It was determined that uranium(VI) which had been extracted into 0.5 M DOSO in 1,2 dichloroethane could be quantitatively recovered by back-extracting three times with a 0.1 M solution of sulfuric acid or two times with 1 M solution.

The effect of perchlorate concentration upon the extraction of uranium(VI) was next studied. Solutions of 0.5 M DOSO in 1,2 dichloroethane were used to extract 0.01 M uranium(VI) from varying concentrations of perchloric acid and lithium perchlorate. The perchloric acid solutions ranged in concentration from 0.05-6.0 M. The lithium perchlorate solutions contained 0.025 M perchloric acid and varied in perchlorate concentration from 0.05 to 4.22 M, the concentration of a saturated solution of lithium perchlorate at 27°C. The results of this study are presented in Figure 33.

The distribution ratios for the perchloric acid solutions, after an initially linear increase, reach a limiting value of 100 at 1-2 M acid and then decrease slightly. This behavior at high perchloric acid

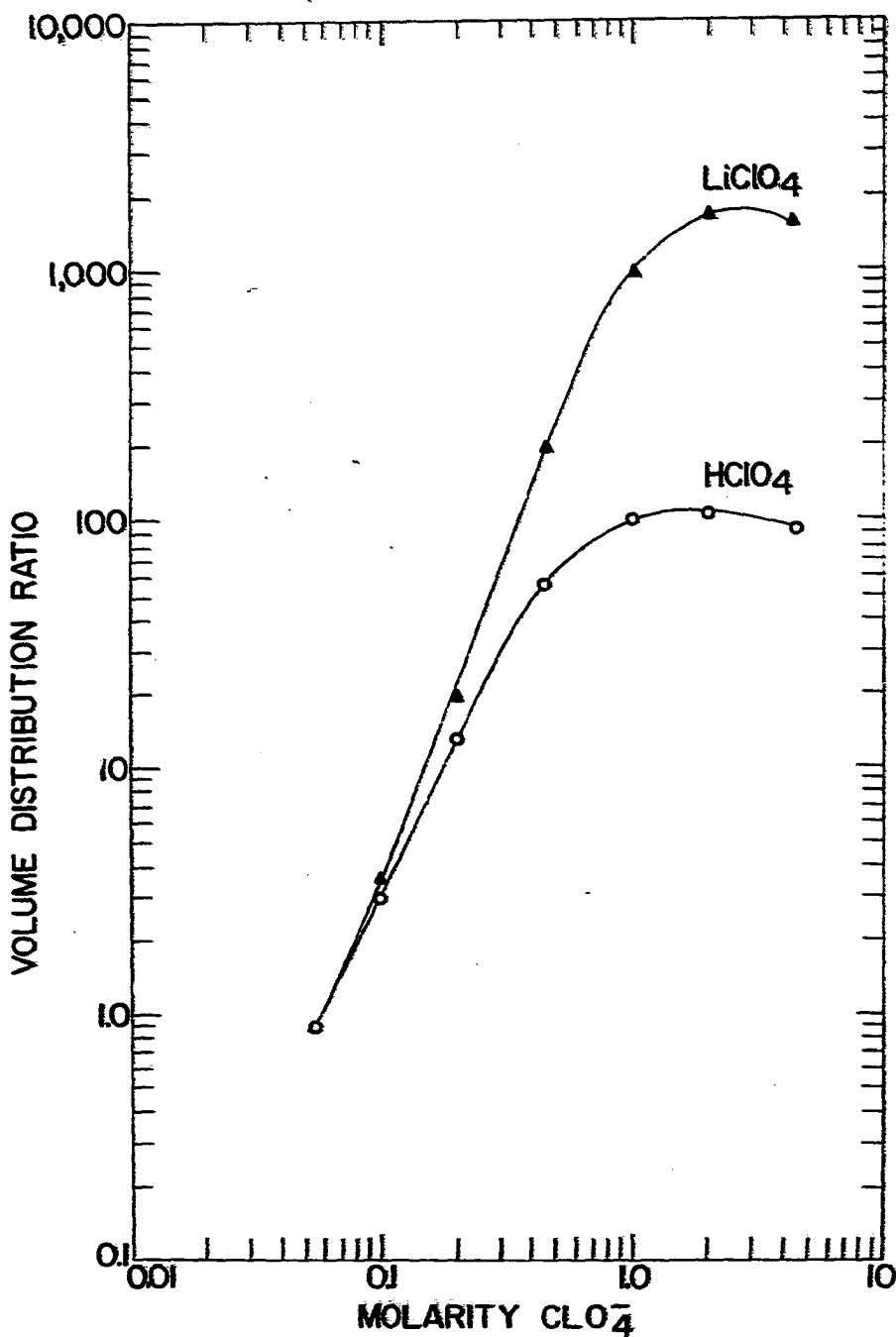
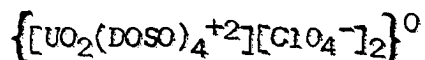


Figure 33. The distribution ratio of uranium(VI) extracted into 0.5 M DOSO 1,2 dichloroethane as a function of the concentration of perchloric acid or lithium perchlorate in the aqueous phase

concentrations is probably due to competitive extraction of the acid by DOSO (46). The linear portion of the curve has a slope of 2.0, confirming that the formula of the extractable complex is;



The curve for the extraction of uranium(VI) from lithium perchlorate at constant hydrogen ion concentration has a longer linear portion than the perchloric acid curve and also a higher slope, 2.6. This curve too deviates from linearity and decreases at higher concentrations of perchlorate, possibly owing to partitioning of lithium perchlorate. At all concentrations above 1 M lithium perchlorate, however, the distribution ratio is greater than 1000, the magnitude necessary for quantitative (99.9%) extraction of uranium(VI). It was decided, therefore, to limit future extraction studies to 1 M lithium perchlorate solutions.

A series of extractions was next performed to determine the effect of hydrogen ion concentration upon the extraction of uranium(VI) from 1 M perchlorate solutions. The solutions (which contained 0.01 M uranium(VI)) were composed of mixtures of lithium perchlorate and perchloric acid. The pH of each solution was measured prior to extraction with 0.5 M DOSO in 1,2 dichloroethane. A plot of distribution ratio as a function of pH is presented in Figure 34.

The distribution ratios for the extraction of uranium(VI) from 1 M perchlorate solution approach a limiting value of about 1900 with decreasing hydrogen ion concentration. The decrease in extraction at low pH is, again, apparently the result of competitive extraction of perchloric acid. These data show that a quantitative extraction of uranium(VI) is possible from 1 M perchlorate solutions of pH 1 or higher.

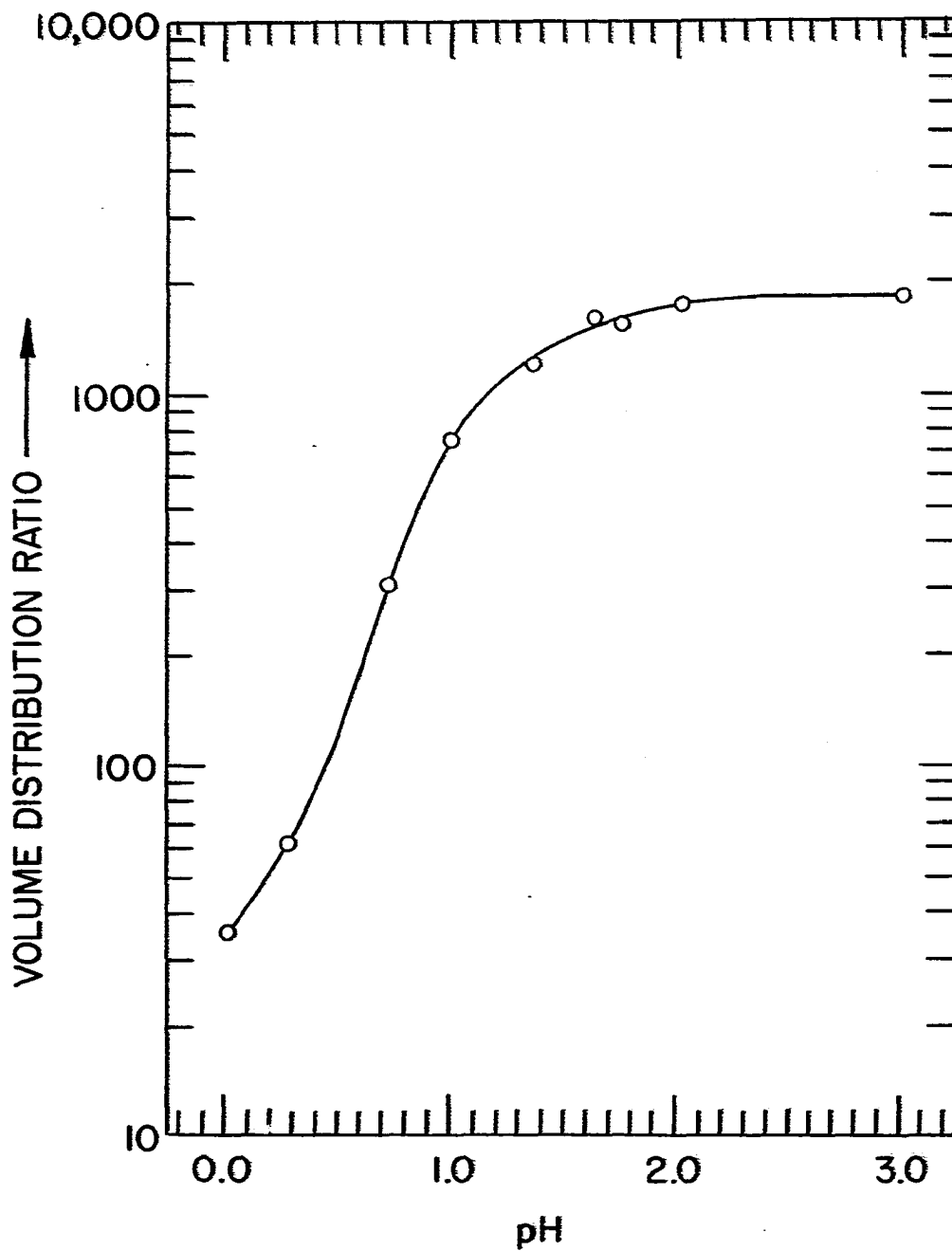


Figure 34. The distribution ratio of uranium(VI) extracted into 0.5 M DOSO in 1,2 dichloroethane from 1.0 M aqueous perchlorate mixtures as a function of the pH of the aqueous phase

On this basis, it was decided to limit future extraction studies to 1 M lithium perchlorate solutions containing 0.025 M perchloric acid (pH 1.65).

A study was next made of the extent of extraction of other metals under the conditions of quantitative extraction of uranium(VI). Solutions of 0.01 M metal in 1.0 M lithium perchlorate-0.025 M perchloric acid were prepared. The metal perchlorate salts were used when possible. Nitrate or chloride salts were used only when it was known that the metals would not form complexes with these anions. For other metals, such as iron(III), palladium(II), gallium(III), etc., where strong complexation by the chloride ion was anticipated, the chloride salts were fumed to near dryness with concentrated perchloric acid and taken up in a solution of 1 M lithium perchlorate. An exception to this procedure was tin(IV). Considerable hydrochloric was required to keep this metal in solution.

The metal solutions were extracted for five minutes with 0.5 M DOSO in 1,2 dichloroethane and the extent of extraction was quantitatively determined. Table 17 lists the metals studied in order of decreasing extraction. The same data are presented in periodic form in Figure 35. A discussion of the analytical significance of these results will be deferred until the next section (Analytical separations).

An examination of the data in Table 17 reveals very few metals, in addition to uranium(VI), which are strongly extracted. Palladium(II) and gold(III) are two notable exceptions. It will be recalled that these two metals were also strongly extracted by DOSO on paper (Figure 19). The behavior of palladium(II) and gold(III) is a further indication

Table 17. The extraction of metals from 1.0 M lithium perchlorate-0.025 M perchloric acid into 0.5 M DOSO in 1,2 dichloroethane

Metal	Percent extraction	Volume distribution ratio
Pd(II) <sup>1</sup>	> 99.99	> 5x10 <sup>5</sup>
U(VI)	99.93	1630
Au(III)	98.7	75.9
Hg(II)	94.4	16.9
Ce(IV) <sup>2</sup>	72.5	2.63
Sc(III)	42.7	0.744
Sn(IV) <sup>3</sup>	31.7	0.464
Ag(I)	28.9	0.406
V(IV)	15.6	0.185
Fe(III) <sup>4</sup>	12.7	0.145
Pb(II)	9.92	0.110
Mo(VI)	9.31	0.103
Th(IV)	8.03	0.0873
In(III)	5.69	0.0604
Ga(III)	5.68	0.0588
Bi(III)	5.46	0.0578
Ti(IV)	2.87	0.0295

<sup>1</sup>In the presence of 0.1 M HCl, kinetics are slow and  $D_v = 530$ .

<sup>2</sup>Reduced slowly to Ce(III).

<sup>3</sup>Hydrochloric acid required to keep Sn(IV) in solution.

<sup>4</sup>In the presence of 0.1 M HCl, % extraction = 35.6%.



Table 17 (Continued)

Metal	Percent extraction	Volume distribution ratio
Lu(III)	1.99	0.0203
Al(III)	0.61	0.0061
Cd(II)	0.55	0.0056
Hf(IV)	0.39	0.0039
Cs(I)	0.28	0.0028
As(III)	0.24	0.0024
Cr(III)	0.19	0.0019
Zn(II)	0.13	0.0013
Ce(III)	0.12	0.0012
Zr(IV)	less than 0.10	less than 0.0010
Ba(II)	"	"
Sr(II)	"	"
Co(II)	"	"
Cu(II)	"	"
Ni(II)	"	"
Mn(II)	"	"
Gd(III)	"	"
Y(III)	"	"
Pt(IV)	"	"
Ru(III)	"	"

of strong sulfur-metal interaction in their complexes. The decrease in the rate and magnitude of extraction of palladium(II) in the presence of dilute hydrochloric acid (footnote 1) shows that DOSO must compete with chloride ions for coordination sites to form the extractable complex. This indicates that the composition of this complex is probably similar to that of uranium(VI), i.e.  $[\text{Pd}(\text{DOSO})_4][\text{ClO}_4]_2$ .

The moderately weak extraction of a number of metals, such as iron(III), gallium(III), lead(II), etc., in the absence of a complexing anion is interesting. Since the extraction necessarily occurs by a mechanism of cation solvation, the sulfoxide-metal ratios in some of the complexes must be quite high. The large size and small coordination number of silver(I) probably accounts for the unexpectedly high extraction of that metal.

Before concluding this section, it should be pointed out that the strong extraction of uranium(VI) from perchlorate solution is not a phenomenon unique to this system. The important step is the formation of the cation  $\text{UO}_2(\text{DOSO})_4^{+2}$ . Once this is accomplished, an anion is needed merely to give charge neutralization and yield an ion-pair that is readily solvated in the organic phase. The perchlorate ion is a fairly good counter ion, but other anions could serve the purpose equally well or better. It might be expected that an organic anion, such as an aromatic sulfonate, would be a better counter ion than perchlorate. This was demonstrated for the case of 2-naphthalene sulfonic acid. Qualitative experiments showed that the extraction by DOSO of uranium(VI) in the presence of this anion was nearly quantitative. Gillette (79) studied the extraction of a number of aromatic sulfonic acids by an analogous

organic cation tricapryl ammonium chloride, a liquid ion exchanger. His results suggest that an anion such as 2,4,6-trinitrobenzene sulfonate would be the best counter ion for the extraction of the uranium(VI)-DOSO cation.

Analytical separations      An examination of the data in Table 17 reveals the great potential of the DOSO-perchlorate system for analytical separations of uranium(VI) from most metals. It can be seen that a single batch extraction will quantitatively separate uranium(VI) from zirconium (IV) → ruthenium(III). A separation from a much larger number of metals is possible using the technique of reversed-phase column chromatography. On such a column, uranium(VI) would be retained (along with palladium(II), gold(III), and, probably, mercury(II)) while cerium(IV) → ruthenium(III) would be rapidly eluted. From Figure 35, it appears certain that the list could be expanded to include the remaining alkali and alkaline earth metals and the lanthanides, thus, allowing a separation of uranium(VI) from nearly 60 other metals. In the work that will be described, however, uranium(VI) was separated from only a few of these metals. Needless to say, those few were carefully selected so as to best demonstrate the utility of this analytical separation system.

One of two columns was used for all separation work. Both employed 0.5 M DOSO in 1,2 dichloroethane sorbed on 60-80 mesh XAD-2 as the stationary phase. One column, 9.0x2.0 cm., was used mainly for the separation of moderate to small quantities of uranium(VI) from other metals. The second column, 10.0x0.6 cm., possessed only 10% of the

Li	Be	ELEMENT										B	C	N	O	F
Na	Mg	Dv										Al(III)	Si	P	S	Cl
		% Extraction										0.008				
												0.61				
K	Ca	Y(III)	Ti(IV)	V(IV)	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ga(III)	Ge	As(III)	Se	Br
		< 0.001	0.030	0.185	0.002	< 0.001	0.145	< 0.001	< 0.001	< 0.001	0.001	0.059		0.002		
		< 0.10	2.87	15.6	0.19	< 0.10	12.7	< 0.10	< 0.10	< 0.10	0.13	5.68		0.24		
Rb	Sr(II)	Sc(III)	Zr(IV)	Nb	Mo(VI)	Tc	Ru(III)	Rh	Pd(II)	Ag(I)	Cd(II)	In(III)	Sn(IV)	Sb	Te	I
		< 0.001	< 0.001		0.103		< 0.001		> 1000	0.408	0.006	0.060	0.464			
		< 0.10	< 0.10		9.31		< 0.10		> 99.9	28.9	0.55	5.69	31.7			
Cs(I)	Ba(II)		Hf(IV)	Ta	W	Re	Os	Ir	Pt(IV)	Au(III)	Hg(II)	Tl	Pb(II)	Bi(III)	Po	At
		0.003	0.004						< 0.001	75.9	16.9		0.110	0.058		
		0.28	0.39						< 0.10	98.7	94.4		9.92	5.46		
Fr	Ra	La	Ce(III)	Pr	Nd	Pm	Sm	Eu	Gd(III)	Tb	Dy	Ho	Er	Tm	Yb	Lu(III)
			0.001						< 0.001							0.020
			0.10						< 0.10							1.99
		Ac	Th(IV)	Pa	U(VI)											
			0.087		> 1000											
			0.03		> 99.9											

Figure 35. The extraction of metals from 1.0 M perchlorate solutions into 0.5 M DOSO in 1,2 dichloroethane

capacity of the first and was mainly used for the separation of trace amounts of uranium(VI) from other metals.

The distribution ratio of uranium(VI) given in Table 17 (although of the magnitude required for a quantitative batch extraction) is much higher than necessary for most reversed-phase column separations. The distribution ratio of 100 attained in 1 M perchloric acid is quite adequate and so, whenever possible, this concentration of acid was used as the eluent for column separations.

The sorption and desorption of uranium(VI) was first studied. It was shown that when  $5.0 \times 10^{-2}$  mmoles of uranium(VI) was sorbed on the large column, no metal could be detected in the effluent during elution with 250 ml. of 1 M perchloric acid. Elution with 100 ml. of 1 M sulfuric acid gave 99.8% recovery\* of the added uranium. Similarly,  $1.87 \times 10^{-3}$  mmoles (0.445 mg.) of uranium(VI) sorbed on the small column was not eluted with 60 ml. of 1 M perchloric acid, but elution with 10 ml. of 1 M sulfuric acid (Figure 36) gave 100.5% recovery of the added uranium. For some analyses, the uranium was desorbed by eluting with 10 ml. of methanol. This procedure also removed the stationary phase, making it necessary to add additional methanol to keep the DOSO in solution during the colorimetric analysis of uranium(VI).

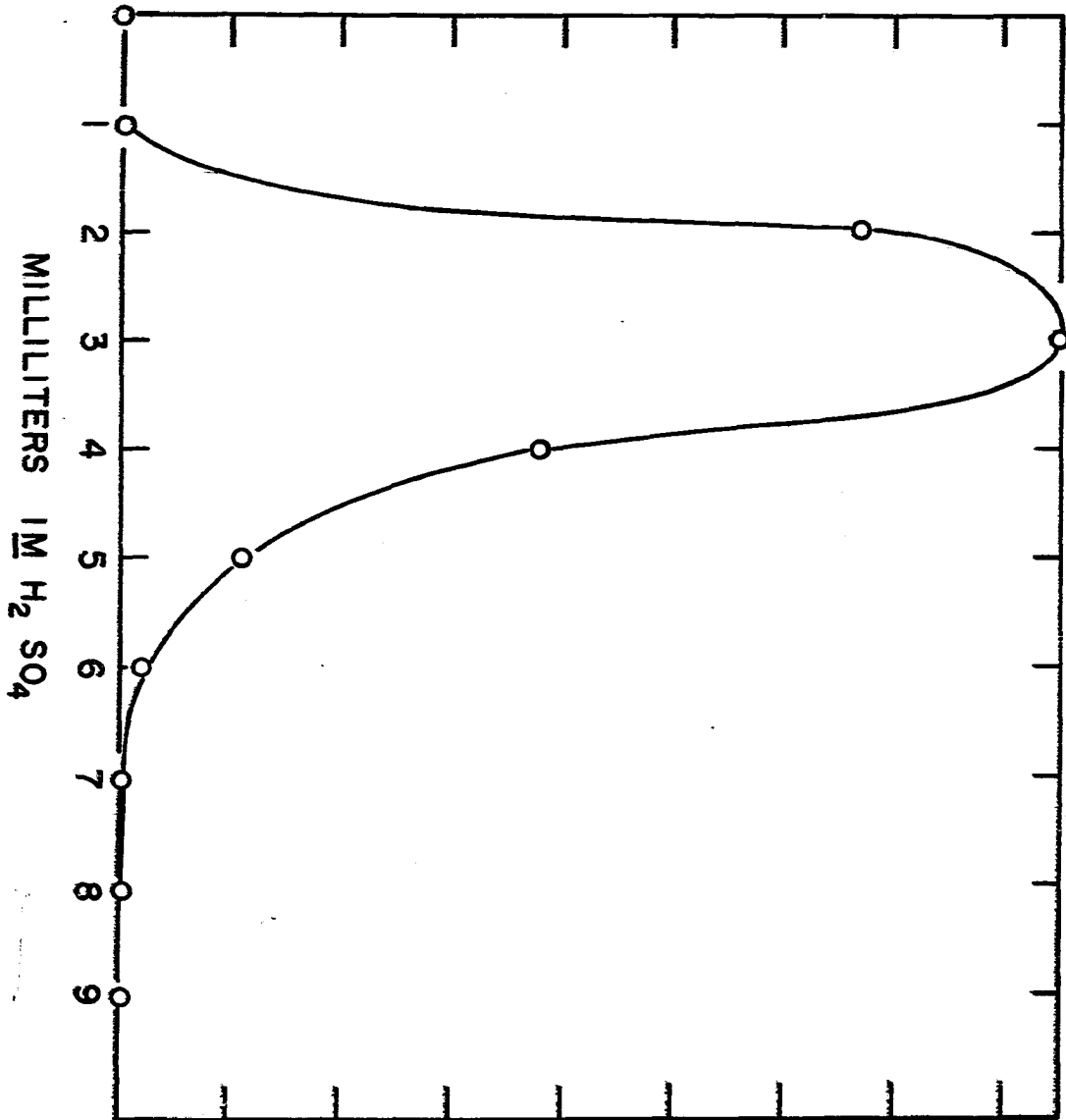
Two experiments were performed in which moderate amounts of uranium (VI) were separated from thorium(IV) and zirconium(IV). Synthetic mixtures which contained 0.05 mmoles of uranium(VI) and 0.25 mmoles of

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\*All analyses for uranium were performed using the Arsenazo I colorimetric method as described under Analytical Procedures.

Figure 36. Curve for the elution of 2.0 micromoles of uranium(VI) from a 10x0.6 cm. column containing 0.5 M DOSO in 1,2 dichloroethane sorbed on 60-80 mesh XAD-2

RELATIVE CONCENTRATION OF U (VI)



the other metals in 1 M perchloric acid were sorbed on the large column. Zirconium(IV) and thorium(IV) were both eluted with 30 ml. of 1 M perchloric acid, while uranium(VI) was eluted as previously described. Table 18 gives the results of these analyses.

Table 18. Separation of uranium(VI) from thorium(IV) and zirconium(IV)

Experiment number	Metal	mmoles added	mmoles found	Percent recovery
1	U(VI)	0.0510	0.0508	99.5
	Th(IV)	0.234	0.233	99.8
2	U(VI)	0.0510	0.0510	100.8
	Zr(IV)	0.266	0.265	99.6

The separation and recovery of small amounts of uranium(VI) from large amounts of other metals was next attempted. Samples of europium oxide, samarium oxide, and anhydrous thorium tetrachloride weighing from three to five grams were dissolved in perchloric acid. After the concentration of acid had been diluted to below 1 M, 0.5-2.4 mg. of uranium was added in the form of a dilute solution of uranyl perchlorate delivered from a microliter buret. Each sample was sorbed onto the large column and eluted with 1 M perchloric acid until no metal could be detected in the effluent by an Arsenazo I spot test. This step usually required about 250 ml. of eluent. The uranium was then eluted, as before, with 100 ml. of 1 M sulfuric acid.

The generally high recovery of uranium in these samples made it necessary to apply a correction for impurities in the eluents and in the samples. New metal samples were prepared, but without adding any



uranium(VI). The separation procedure was repeated with the same volume of 1 M perchloric acid and sulfuric acid as was previously used for that metal. The sulfuric acid effluent was analyzed by the Arsenazo I method and any net absorbance (regardless of its actual origin) was reported as a weight of uranium(VI). This quantity was then subtracted, as a blank, from the amount of uranium(VI) found in the first sample. This corrected amount of uranium(VI) was compared to the amount added to determine the extent of recovery.

A "column" blank was also measured to determine how much interference arose from the reagents used, and how much was inherent in the samples. The column was eluted with the same volumes of eluents previously used and the sulfuric acid fraction was analyzed. Again, any net absorbance was reported as a weight of uranium(VI). The results of these analyses are presented in Table 19.

An examination of the data in Table 19 reveals that the blank associated with the eluents is quite constant and fairly low. The blanks associated with the samples, however, are quite variable. One is naturally tempted to ascribe these blanks to the presence of small amounts of uranium in the samples. This is not an unreasonable assumption, owing to the high degree of specificity of the separation system for uranium(VI). However, the presence of gold(III), palladium(II) or mercury(II) in the samples, although certainly less probable than the presence of uranium, could also be responsible. Alternatively, the high results might simply be due to incomplete separation, as the other metals all interfere with determination of uranium(VI) at pH 7. For the case of thorium tetrachloride, however, this possibility has been

Table 19. Separation of small amounts of uranium(VI) from thorium(IV), samarium(III), and europium(III)

Experiment number	Separation number	Sample	Sample weight (g.)	Uranium added (mg.)	Gross uranium found (mg.)	Net uranium found (mg.)	Recovery of added uranium
I	1	Column blank	---	---	0.05	---	---
	2	Sm <sub>2</sub> O <sub>3</sub>	3.49	---	0.18	0.13	---
	3	Sm <sub>2</sub> O <sub>3</sub>	3.49	2.40	2.39	2.26	-6.0%
II	1	Column blank	---	---	0.057	---	---
	2	Eu <sub>2</sub> O <sub>3</sub>	3.52	---	0.078	0.021	---
	3	Eu <sub>2</sub> O <sub>3</sub>	3.52	0.480	0.547	0.469	-2.3%
II	1	Column blank	---	---	0.06 <sup>1</sup>	---	---
	2	ThCl <sub>4</sub>	4.47	---	0.25 <sup>2</sup>	0.19	---
	3	ThCl <sub>4</sub>	4.47	2.40	2.83 <sup>1</sup>	2.58	+7.0%

<sup>1</sup>Average of two separations.

<sup>2</sup>Average of three separations.

eliminated. The sample "blanks" gave no net absorbance with Arsenazo I at pH 2, showing that a metal other than thorium(IV) was responsible for the original absorbance at pH 7.

However, a strong claim for uranium impurities in the samples cannot be made without the support of an alternative method of analysis. It was to this end that the next series of experiments was directed.

Five separations of uranium(VI) from thorium(IV) were performed

using a new sample of anhydrous thorium tetrachloride. For each determination, 5.00 g. of salt were dissolved in 1 M perchloric acid or, when the small column was used, 0.9 M lithium perchlorate-0.1 M perchloric acid. The samples were sorbed onto the columns and the thorium(IV) was completely eluted with the appropriate perchlorate solution. The columns were then eluted with either 1 M sulfuric acid or methanol and the effluents were analyzed by the Arsenazo I method.

The amount of metal, as uranium(VI), in each of the thorium tetrachloride samples was then calculated by subtracting a column blank from the value initially determined. For separations where a known amount of uranium(VI) had been added to the sample, this amount was also subtracted. The results of these analyses are presented in Table 20.

The data in Table 20 indicate that a small amount of impurity, assumed to be uranium(VI), is present in the sample of thorium tetrachloride. Owing to the much smaller magnitude of the column blank and the smaller amount of uranium(VI) added, the values obtained in experiment III are probably most accurate.

It remained to be demonstrated that the metallic impurity in the samples which was being retained on the columns was indeed uranium(VI), and, if so, whether it was present in the amount determined by the separation method. Neutron activation analysis was the technique chosen to confirm the analyses.

A 10.0 g. sample of the thorium tetrachloride dissolved in 50 ml. of 0.9 M lithium perchlorate-0.1 M perchloric acid, was extracted in a separatory funnel with 10 ml. of 0.5 M DOSO in 1,2 dichloroethane. The organic phase was removed and back-extracted five times with fresh

Table 20. Analysis of 5.00 gram samples of thorium tetrachloride for trace amounts of uranium(VI)

Experiment number	Size of column used	Uranium eluted with	Column blank obtained (mg. U(V), ppm U(VI))	Separation number	Uranium added (mg.)	Gross uranium recovered (mg.)	Net uranium(VI), in thorium tetrachloride (corrected for uranium added and/or column blank) (mg.)	(ppm.)
I	10.0 x 2.0 cm.	100 ml. 1 M H <sub>2</sub> SO <sub>4</sub>	0.080,	1	---	0.120	0.040	8.0
			16.0 ppm	---	---	---	---	---
II	10.0 x 0.6 cm.	10 ml. 1 M H <sub>2</sub> SO <sub>4</sub>	0.030,	1	---	0.066	0.036	7.2
			6.0 ppm	2	0.480	0.404	0.030	6.0
III	10.0 x 0.6 cm.	10 ml. methanol	0.006,	1	---	0.028	0.021	4.2
			1.2 ppm	2	0.055	0.075	0.020	4.0

portions of the perchlorate solution until no thorium(IV) could be detected in the aqueous phase. The organic phase was again removed, the solvent was evaporated, and the solid DOSO was sealed in a polyethylene vial. Four additional samples of DOSO in vials were prepared for use as standards and a blank. To these vials were added the amounts of uranium (VI) equivalent to 48 ppm., 4.8 ppm., 0.48 pp., and 0.00 ppm. of uranium in 10 g. of thorium tetrachloride. The five vials were then analyzed by neutron activation analysis using the procedure described on page 42.

The presence of uranium in the extractable complex was easily identified from the complicated mixture of activities arising from the fissioning of  $U^{235}$  and also from the activity of  $Np^{239}$  produced from the neutron capture of  $U^{238}$ . The fission products used to identify the presence of uranium are listed in Table 21. The fission products used for the quantitative analysis of uranium, along with the results obtained, are given in Table 22.

Table 21. Nuclides employed for qualitative identification of uranium in DOSO used to extract a 10 g. sample of thorium tetrachloride

Nuclide	Half-life	Gamma ray energies used (Mev.). Literature values (80) are in parentheses
$Np^{239}$	2.35 days	0.231(0.223), 0.278(0.278)
$La^{140}$	40 hours	0.477(0.478), 0.327(0.330)
$Pr^{142}$	19.2 hours	1.575(1.580)
$Ce^{142}$	33 hours	0.295(0.294)

Table 21 (Continued)

Nuclide	Half-life	Gamma ray energies used (Mev.). Literature values (80) are in parentheses
Y <sup>93</sup>	10.1 hours	0.267(0.265)
Tc <sup>95</sup>	20 hours	0.776(0.768)
Ru <sup>97</sup>	2.9 days	0.219(0.217), 0.324(0.323)
Md <sup>99</sup> -Tc <sup>99m</sup>	66 hours	0.142(0.142)

Table 22. Analysis of trace amounts of uranium in DOSO used to extract a 10 g. sample of thorium tetrachloride

Nuclide	Half-life	Energy of photo-peak counted (Mev)	Uranium in original ThCl <sub>4</sub> sample (ppm)
Np <sup>239</sup>	2.35 days	0.231	7.5
Pr <sup>142</sup>	19.2 hours	1.575	4.3
Y <sup>93</sup>	10.1 hours	0.267	3.0
Ce <sup>142</sup>	33 hours	0.295	2.2
La <sup>140</sup>	40 hours	0.477	1.1
			Average = 3.6 ppm

The results of the neutron activation experiment are a reasonable confirmation of the validity of the results of the analyses presented in Table 20. It is anticipated that similar experiments might also provide confirmation of the results presented in Table 19.

Conclusions It is felt that the DOSO-perchlorate separation system will be very useful for the analysis of uranium in a wide range of materials. The solvent extraction behavior of uranium(VI) has probably been more extensively studied than that of any other metal. However, out of the impressive number of systems that have been described for the analytical separation of uranium, few other methods are able to combine the very high extent of extraction of uranium(VI) with the high degree specificity that is observed in the present system.

The most nearly comparable analytical method is that described by Fritz and Schmitt (81). These authors report the separation of uranium(VI) from a large number of other metals using partition chromatography. Uranium(VI) is rapidly eluted by methyl isobutyl ketone from a silica gel column containing 6 M nitric acid as the stationary phase. Very few other metals are extracted under these conditions allowing a rather selective elution of uranium. The metals remaining on the column can then be readily eluted with 6 M nitric acid. Their method is most applicable to the analysis of small amounts of other metals in a uranium matrix. The present method, however, would be best applied to the analysis of small amounts of uranium in other materials.

Finally, it should be pointed out that most observations regarding the separation of uranium(VI) from other metals also apply to palladium(II). Although the work described here has been only concerned with uranium(VI), the even stronger interaction of DOSO with palladium(II) endows this system with an equal analytical potential for that metal.

SUMMARY

The sulfoxides, a new class of solvent extraction reagents, were evaluated for use in the separation of metal ions. The compounds most extensively studied were di-n-octyl sulfoxide, p-tolyl sulfoxide, and two previously unreported bifunctional sulfoxides; bis(n-octylsulfinyl) methane and bis(n-octylsulfinyl)ethane.

Using the rapid, qualitative technique of reversed-phase paper chromatography, the interactions of these sulfoxides with some 50 metal ions were investigated in several acid-ligand systems. All four reagents were studied in 1-10 M hydrochloric acid and 1-11 M nitric acid. Di-n-octyl sulfoxide and bis(n-octylsulfinyl) methane were also studied in perchloric acid and in ammonium thiocyanate-perchloric acid mixtures.

From this survey, those systems which showed the greatest potential for analytical or large-scale separations or which demonstrated behavior of a fundamental interest to the understanding of sulfoxide-metal interactions were selected for more rigorous study. Liquid-liquid solvent extraction and reversed-phase column chromatography were the techniques most extensively employed in this second stage of evaluation.

From these data, several analytical separation systems were devised. To demonstrate the utility of these systems, a number of metal combinations were quantitatively separated by batch extraction or by reversed-phase column chromatography. Some of the more interesting features of this investigation are detailed below.

1. For monofunctional sulfoxides, evidence of four distinct mechanisms of extraction was observed.



- a. Solvation of neutral, metal-ligand complexes.
  - b. Solvation of cations followed by ion-pair formation.
  - c. One of the above, but resulting from coordination through the sulfur atom of the sulfoxide group, rather than through the oxygen atom.
  - d. Solvation of certain metals involving the aromatic ring of p-tolyl sulfoxide.
2. It was observed that, as predicted, bis(n-octylsulfinyl)methane and bis(n-octylsulfinyl)ethane exhibit bidentate in the extraction of certain metals. This type of interaction was most evident in the extraction of lanthanides from nitric acid. The extraction of the series of lanthanides was unexpectedly observed to go through a maximum near europium. This phenomenon, and the generally ineffective chelation of bis sulfoxides compared to bis phosphine oxides, was rationalized in terms of steric hindrance.
  3. Titanium(IV), zirconium(IV) and thorium(IV) were quantitatively separated by reversed-phase column chromatography. Thorium(IV) and zirconium(IV) were also separated quantitatively by a single batch extraction.
  4. Zirconium(IV) and hafnium were quantitatively separated from each other by batch extractions and by reversed-phase column chromatography. Hafnium(IV) was also quantitatively separated from a 5,000 fold excess of zirconium(IV).
  5. An analytical system was studied in detail which permits the separation of uranium(VI) from most metals. Of the over 50

metals studied, palladium(II), gold(III) and mercury(II) are the only possible interferences. Using reversed-phase column chromatography, trace amounts of uranium were quantitatively separated from thorium(IV) and certain lanthanides. During this investigation, the composition of the extractable uranium complex was established.

6. The existence of many other potential solvent extraction separation systems was observed and basic conditions for their development were described.

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