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SOME BIS(DIALKYLPHOSPHINYL)METHANES AS SOLVENT EXTRACTANTS

by

James Roger Parker

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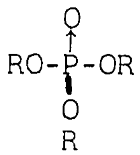
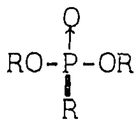
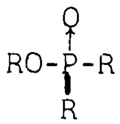
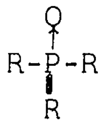
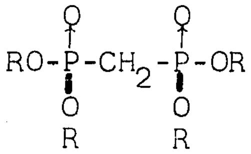
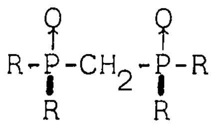
INTRODUCTION

General interest in neutral organophosphorus compounds as extractants began in 1949. At that time Warf (1) reported that uranium(VI) nitrate, thorium nitrate, and cerium(IV) nitrate were readily extracted by tri-n-butyl phosphate. As other neutral organophosphorus extractants were investigated, it quickly became apparent that there was a relationship between extracting ability and phosphoryl basicity (2, 3). The more basic type of compound was the better extractant. Thus, as expected, extracting ability followed the order phosphine oxides, R_3PO, > phosphinates, $(RO)R_2PO$, > phosphonates, $(RO)_2RPO$, > phosphates, $(RO)_3PO$. The structures of some neutral organophosphorus extractants are given in Table 1.

The search for good extractants for elements such as uranium which are of such importance to the atomic energy program did not stop here. A diphosphoryl phosphine oxide, bis(di-n-hexylphosphinyl)methane, $R_2P(O)CH_2P(O)R_2$, was synthesized by Richard et al. (4) in the hopes that it might be a chelating agent and, therefore, an even better reagent than a monodentate ligand. It was found (5, 6) that it was indeed a superior extractant for uranium and probably for other metals. Whether or not it is a chelating agent is still in doubt.

Table 1. Structures of some neutral organophosphorus extractants

Structure	Name
 $\mathrm{RO-}\underset{\underset{\mathrm{R}}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-OR}$	trialkyl phosphate
 $\mathrm{RO-}\underset{\mathrm{R}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-OR}$	dialkyl alkylphosphonate
 $\mathrm{RO-}\underset{\mathrm{R}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-R}$	alkyl dialkylphosphinate
 $\mathrm{R-}\underset{\mathrm{R}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-R}$	trialkylphosphine oxide
 $\mathrm{RO-}\underset{\underset{\mathrm{R}}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-CH_2-}\underset{\underset{\mathrm{R}}{\mathrm{O}}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-OR}$	bis(dialkoxyphosphinyl)methane
 $\mathrm{R-}\underset{\mathrm{R}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-CH_2-}\underset{\mathrm{R}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{P}}}\mathrm{-R}$	bis(dialkylphosphinyl)methane

In investigations with different types of organophosphorus compounds, it was often found that compounds with branched-chain alkyl groups were more selective reagents than those with straight chains. For instance, Siddall (7) found in his study on trialkyl phosphates that the extraction of thorium nitrate is greatly decreased when bulky alkyl groups (branched-chain groups) are in the extractant molecule. At the same time the extraction of neptunium(IV and VI), plutonium(IV and VI), and uranium(VI) is relatively unaffected. Ross and White (8), while studying the trialkylphosphine oxides, discovered that tris(2-ethylhexyl)phosphine oxide would not extract chromium(VI) from 1 _M_ nitric acid, indium from 1 _M_ sulfuric acid, thorium from hydrochloric acid, perchloric acid, or sulfuric acid, or vanadium(IV) from 7 _M_ hydrochloric acid. On the other hand, tri-_n_-octylphosphine oxide did extract these elements under the given conditions.

With these ideas in mind, it was decided to investigate some of the solvent extraction properties of several branched-chain bis(dialkylphosphinyl)methanes and to compare them with related compounds. This thesis presents the results and conclusions of that investigation.

REVIEW OF LITERATURE

Tri-n-butyl Phosphate as a Solvent Extractant

This review, as well as those to follow, deals primarily with the extraction of metal nitrates unless otherwise mentioned.

Tri-n-butyl phosphate, TBP, has been studied much more extensively than any of the other organophosphorus extractants and, indeed, probably more than any other extractant. TBP has a dielectric constant of about 8 (9). Electrolytes are essentially unionized in pure TBP or in dilute solutions of TBP (10). There is evidence that electrolytes may ionize in hydrated TBP or in concentrated solutions of TBP (11, 12). Its high dipole moment of 3.0-3.1 Debyes (9, 13) accounts for its ability to form ion pairs or coordination complexes with many inorganic salts. It is nonvolatile at room temperature and has a wide liquid range with a melting point less than -80°C (10) and a boiling point of 289°C at 760mm (decomposition) (14). Its solubility in water is 0.4 g/l at 25°C (15-18). Its high viscosity (33.2 millipoise) (19) and the closeness of its density (0.973 g/ml at 25°C) (14, 19) to that of water make it desirable to use a diluent. Use of a diluent also gives increased selectivity. Common diluents are heptane, benzene, kerosene, carbon tetrachloride, and n-butyl ether. It has been shown that aromatic and aliphatic hydrocarbons are generally the best diluents (20-26). Temperature increases usually cause a decrease in distribution coefficients (27-35).

The elements which are well extracted include gold(III), uranium(VI), plutonium(IV and VI), neptunium(IV and VI), thorium, zirconium, hafnium, cerium(IV), and others depending upon the conditions used. A summary of some distribution coefficients obtained by Ishimori and Watanabe (36) for the extraction of metal nitrates by 100% TBP is given in Table 2.

TBP forms a monohydrate with water with dilute solutions of TBP in organic solvents. At concentrations of TBP greater than about 0.1 M, other species may be present such as $H_2O \cdot 2TBP$. The infrared spectra of the system TBP-water has been interpreted as indicating weak hydrogen bonding between the phosphoryl groups and the water molecules (15, 37, 38). Whitney and Diamond (39) have presented equilibrium data to show that the hydrate is of the form $TBP \cdot H_2O$ for concentrations of TBP up to 0.1 M. Bullock and Tuck (40) using nuclear magnetic resonance techniques found the system to be quite complicated. The 1:1 ratio of TBP to water at saturation is not interpreted by these authors as indicating discrete $TBP \cdot H_2O$ molecules. They prefer to view the TBP-water system as involving an equilibrium between $(TBP)_2 \cdot H_2O$, $(TBP)_3 \cdot 2H_2O$, and ring polymers $(TBP)_{n+1} \cdot nH_2O$. Chaikhorskii et al. have determined the thermodynamic quantities for the formation of $TBP \cdot H_2O$ (41). Olander and Benedict (42) view the dissolving of water in TBP as a mass transfer process involving no

Table 2. Extraction of metal nitrates by tri-*n*-butyl phosphate (36)

Distribution coefficient[a]	Element		
10^3 to 10^4	Au(III)		
10^2 to 10^3	Pu(VI)	Np(VI)	Os(VI)
	W(VI)	Tc(VII)	
	U(VI)	Re(VII)	
10^0 to 10^1	Th	Pa	Np(IV)
	Bi	Pd	Hg(II)
	Ru(IV)	Pt	
10^{-1} to 10^0	Po	As(V)	Y
	Ir	Tl(III)	
	Sc	Nb	
10^{-2} to 10^{-1}	La	Pb	Te(VI)
	Ag	Mo(VI)	
	Np(V)	Ra	
10^{-3} to 10^{-2}	Ca	Al	Cu(II)
	Ti	Cd	In
	Fe(III)	Sr	Cs
	Cr(III)	Na	Ba
	Mn(II)	Co	K
10^{-4} to 10^{-3}	Ni	Mg	Zn
	Ga	Ta	

[a] Tracer concentrations of metal in 1 *M* nitric acid extracted with 100% tri-*n*-butyl phosphate.

complexation.

Dilution data show that lithium extracts as $LiNO_3 \cdot 2TBP$ (43). Saturation experiments give a ligand:metal ratio of 2.6:1 at 25°C and 2.2:1 at 50°C (44). Sodium extracts as $NaNO_3 \cdot 3TBP$ (43, 45). Cobalt also forms a trisolvate (45). Copper is reported to form the complex $Cu(NO_3)_2 \cdot 3TBP \cdot H_2O$ in kerosene (46). Nadig (47) assumes the formation of $Cu(NO_3)_2 \cdot 2TBP$ because the solubility of copper(II) nitrate in TBP at saturation is greater than that calculated for $Cu(NO_3)_2 \cdot 3TBP$. The saturation of TBP with $Cu(NO_3)_2$ gives a ligand:metal ratio of 2.8:1 at 25°C (44).

Trivalent metals form trisolvates with TBP. Partition data have confirmed this for yttrium (43, 48), cerium (43, 48, 49), promethium (43), europium (43, 48), terbium (43), thulium (43), lutetium (43), americium (43), and plutonium (50). Hesford has proposed that all the lanthanides form anhydrous trisolvates (51). Solubility data indicate the presence of $Ce(NO_3)_3 \cdot 3.1TBP$ (44) and $Fe(NO_3)_3 \cdot 3TBP$ (47) in saturated solutions of these salts in TBP at 25°C.

Tetravalent metals probably extract as disolvates of TBP although other solvates have been reported and should be considered. Dilution data which agree with the formation of a disolvate have been reported for zirconium (43, 44, 52-54), hafnium (55, 56), neptunium (43), plutonium (32, 43, 57), and thorium (43, 58-61). Solovkin (62) reported that the solvation number of zirconium with TBP varies from 1.0 to 1.8 and isolated a solid complex of the composition $Zr(NO_3)_4 \cdot TBP$. Egorov et al. (63) give $M(NO_3)_4 \cdot TBP$ and $M(NO_3)_4 \cdot 2TBP$ as the extractable species for zirconium and hafnium at low acid concentration and $H_2M(NO_3)_6 \cdot 2TBP$ at high acid concentration. Murbach (64) measured the formation constant for $Zr(NO_3)_4 \cdot 3TBP$. Tsvetkova et al. (65), believe the extractable species to be $Zr(NO_3)_4 \cdot 4HNO_3 \cdot TBP$ and $Zr(NO_3)_4 \cdot 2HNO_3 \cdot TBP$. Peppard et al. (54) found the solvation number of thorium, zirconium, and scandium to vary with nitric acid concentration being 2 at 1.9 M, 3 at 6.13 M, and 4 at 10.1 and 13.8 M. Hesford et al. (66) report the solvation number of thorium to be 2 in 4.5 and 16 M nitric acid and 3 in 10 M nitric acid. Solvation numbers obtained at high acid concentrations by equilibrium methods cannot be considered reliable because of the non-ideality of the systems. The saturation of TBP with $Th(NO_3)_4$ gives a ligand:metal ratio of 2.5:1 at 26.4°C and 2.0:1 at 103-130°C (44). Cryoscopic molecular weight determinations of TBP saturated with $Th(NO_3)_4$ indicate a mixture of species to be present, $Th(NO_3)_4 \cdot 2TBP$ and $Th(NO_3)_4 \cdot 3TBP$ (67. 68). Nadig believes on the basis of infrared evidence that only a single species exists, $Th(NO_3)_4 \cdot 2TBP$ (47).

The hexavalent actinides extract as disolvates. Plutonium forms the complex $PuO_2(NO_3)_2 \cdot 2TBP$ (43, 57, 69, 70) and neptunium the complex $NpO_2(NO_3)_2 \cdot 2TBP$ (43). The formation of $UO_2(NO_3)_2 \cdot 2TBP$ was proposed by Moore (71) and has been confirmed by many workers (38, 43, 45, 72-78). Equilibrium constants have been calculated for the reaction of uranyl nitrate with TBP (74, 79-82) and thermodynamic quantities have been determined (30, 32, 35). Salt effects (79, 83-87), solvent effects (20-23), temperature effects (28, 33, 34, 85, 88), and competing anion effects (89, 90) for the extraction of uranium by TBP have also been studied.

The complex formed when TBP is saturated with uranium(VI) nitrate has the composition $UO_2(NO_3)_2 \cdot 2TBP$ (0°-50°C) and furthermore has a sharp melting point of -6.0 ± .5°C (44). However, it should be noted that saturation of a solution of TBP in 1,2-dichloroethane with uranium(VI) nitrate results in a ligand:metal ratio of 1.4:1 (91). Solovkin found the formation of $HUO_2(NO_3)_3 \cdot 2TBP$ as a third phase when using high concentrations of nitric acid and TBP (92). On the other hand Healy and McKay found no evidence for the extraction of species such as $H_3Nd(NO_3)_6$, $HUO_2(NO_3)_3$, or $H_2Pu(NO_3)_6$ (44).

Chromium(VI) is extracted as trisolvated chromic acid (93). Molybdenum forms an orange-yellow oil with TBP having the composition $H_2MoO_6 \cdot 4TBP$ (50). Rhenium is extracted as $HReO_4 \cdot 3TBP$ (39, 94) or as $HReO_4 \cdot 4TBP$ (95). The extraction of ruthenium appears to be quite complicated with the nature of the extractable species depending upon the conditions. At low acid concentrations the complex $RuNO(NO_3)_3 \cdot 2TBP$ is extracted (96-98) while at higher acid concentrations $HRuNO(NO_3)_4$ and

$H_2RuNO(NO_3)_5$ are extracted (29, 99).

Karl Fischer titrations have shown that lithium nitrate, calcium nitrate, and copper(II) nitrate are hydrated in TBP while cerium(III) nitrate, cerium(IV) nitrate, thorium nitrate, and uranium(VI) nitrate are anhydrous in TBP (44). Infrared spectra have been interpreted as indicating that lithium, magnesium, nickel(II), iron(III), and chromium(VI) nitrates are hydrated in TBP while thorium and uranium(VI) nitrates are anhydrous (37).

It is generally agreed that nitric acid and TBP form the complex $HNO_3 \cdot TBP$ (11, 12, 15, 32, 35, 63, 72, 100-109). This species is most likely anhydrous, although a hydrated species may also exist (11, 15, 77, 104, 110). A complex $HNO_3 \cdot 2TBP$ has been proposed to exist in the presence of the 1:1 complex (27, 63, 77, 103). Also, it is possible to extract nitric acid in amounts greater than can be accounted for by the presence of only a 1:1 complex. Some workers have proposed additional complexes such as $2HNO_3 \cdot TBP$ (27, 63, 72, 102, 104, 111), $2HNO_3 \cdot TBP \cdot H_2O$ (110), $3HNO_3 \cdot TBP$ (105, 111, 112), $3HNO_3 \cdot TBP \cdot H_2O$ (110), and $4HNO_3 \cdot TBP$ (110, 111). Others noting that concentrated aqueous solutions of nitric acid contain a large fraction of unionized nitric acid molecules have postulated the distribution of these unionized molecules into the organic phase unsolvated by TBP in addition to the 1:1 complex (15, 100, 101) or in addition to the $HNO_3 \cdot TBP$ and $3HNO_3 \cdot TBP$ complexes (105).

In the species $HNO_3 \cdot TBP$ the nitric acid molecule is bonded to the phosphoryl oxygen. For species such as $3HNO_3 \cdot TBP$ there is disagreement as to whether the two additional nitric acid molecules are bonded to the oxygens in the alkoxy groups (107, 108, 111) or to the nitrate oxygens (104). As nitric acid is extracted by a solution of TBP in an organic diluent, the water content of the organic phase decreases until the acid concentration in the organic phase equals that of the TBP. The extraction of nitric acid in excess of that required for complete formation of $HNO_3 \cdot TBP$ is accompanied by an increase in the water content of the organic phase. This may indicate the formation of first the anhydrous 1:1 complex and then hydration of that complex and of the nitric acid extracted in excess of the 1:1 complex. Conductivity (12, 44) and infrared (38, 104, 113) measurements indicate that nitric acid is mostly unionized in TBP. Tuck (107) found infrared bands for ionic nitrate, but he used alkaline halide cell windows and his results are, therefore, unreliable.

Formation constants have been measured for $HNO_3 \cdot TBP$ (15, 27, 58, 80, 81, 101, 106) and for $2HNO_3 \cdot TBP \cdot xH_2O$ (27, 83, 102, 110). Thermodynamic calculations have been made for the reaction of nitric acid with TBP to form $HNO_3 \cdot TBP$ (35). Table 3 gives a list of references to reports on the interaction of TBP with various substances. Papers dealing primariliy with one element or group of elements often contain information

Table 3. References to TBP complexes and its uses in extractions

Substance extracted or complexed	References
water	15, 37, 40-42, 114
nitric acid	11, 12, 27, 32, 35, 36, 44, 57, 63, 72, 77, 80, 81, 86, 100-111, 113, 115-120
nitrous acid	121
lithium	43, 44
sodium	43, 45
cesium	122
calcium	43, 44, 84, 123
strontium	44, 84, 122
zirconium	21, 23, 33, 44, 52-54, 62-64, 84, 122-127
hafnium	55, 56, 63, 123-125, 127
thorium	24, 44, 54, 58-61, 66-68, 84, 119, 124, 128-144
cerium	21, 23, 44, 49, 145-147
vanadium	148, 149
niobium	21, 84, 122, 127, 150, 151
tantalum	127
chromium	93, 152
rhenium	39, 94, 95
iron	135, 152, 153
aluminum	44, 135
nickel	152
copper	44, 152, 154
ruthenium	29, 33, 84, 96-99, 155, 156
cobalt	157
scandium	54
yttrium	48, 138, 158-160
rare earths	24, 48, 51, 122, 129, 134, 136-138 159-182

Table 3. (Continued)

Substance extracted or complexed	References
protactinium	134, 183, 184
uranium	11, 20-23, 28, 30, 32-35, 38, 44, 45, 71-93, 116-119, 135-137, 141, 152, 154, 185-193
neptunium	26, 83
plutonium	21, 23, 31, 33, 34, 44, 46, 57, 66, 70, 83, 84, 93, 154, 185, 194
americium	195, 196
actinides	54, 57, 66, 83, 118, 174, 175, 195, 197-199

about related elements. Ishimori and Watanabe (36) give distribution coefficients for almost all the elements as a function of nitric acid concentration.

Tri-n-octylphosphine Oxide as a Solvent Extractant

Tri-n-octylphosphine oxide, TOPO, is a white waxy material melting at 51-52°C (200). A melting point of 59.5-60°C has been reported, but this possibly could be the result of a misprint (201). Its boiling point is 200°C at 0.1 mm (200). Its solubility in water is 1.5 mg/l at 25°C (202). As with TBP, nonpolar diluents are used. Common diluents used include cyclohexane, toluene, kerosene, benzene, and carbon tetrachloride. White and Ross (200) prefer cyclohexane because of its low solubility in water and its ultraviolet spectral characteristics.

White and Ross (200, 203, 204) have summarized most of the known information concerning extractions with TOPO. Ishimori et al. (201) have determined distribution coefficients for the extraction of most elements from hydrochloric and nitric acids with TOPO. A summary of their data on metal nitrates is given in Table 4.

White and Ross (200) report that water is only very slightly soluble in solutions of TOPO in cyclohexane. Nitric acid forms a 1:1 complex with TOPO and possibly a complex $2HNO_3 \cdot TOPO$ (205) or else acid which is extracted in excess of that required for complete formation of the 1:1 complex merely dissolves (206). Other metal nitrate complexes which have been reported include $Zr(NO_3)_4 \cdot 2TOPO$ (207), $Th(NO_3)_4 \cdot 3TOPO$ (205, 208), $Pu(NO_3)_4 \cdot 2TOPO$ (206), $PuO_2(NO_3)_2 \cdot 2TOPO$ (206), and $UO_2(NO_3)_2 \cdot 2TOPO$ (200). Some elements extract as acidic species such as $H_2Cr_2O_7 \cdot 2TOPO$ (209), $HTcO_4 \cdot 2TOPO$ (210), and $H_2Ce(NO_3)_6 \cdot 2TOPO$ (200).

TBP is frequently used as a processing reagent by the chemical engineers. TOPO is too expensive to be used in that manner and it is more commonly employed as an analytical reagent. After an element is extracted by TOPO it may be stripped from the organic phase and then determined (200). Sometimes it is more convenient to determine the element colorimetrically directly in the organic phase (200).

Table 4. Extraction of metal nitrates by tri-*n*-octylphosphine oxide (201)

Distribution coefficient[a]	Element		
10^3 to 10^4	U(VI)		
10^2 to 10^3	Au(III)	Pa	
10^1 to 10^2	Th	Hf	
10^0 to 10^1	Zr	Bi	Sc
	Hg(II)		
10^{-1} to 10^0	Os(VI)	Nb	Dy
	W(VI)	Eu	
	V	Sn	
	Mo(VI)	Pr	
10^{-2} to 10^{-1}	Tl(III)	In	Ni
	Re(VII)	Ta	Ti
	Pd	Pb	Lu
	Y	Cd	Tm
10^{-3} to 10^{-2}	La	Fe(III)	As(V)
	Ag	Ir	
	Pt	Mg	
10^{-4} to 10^{-3}	Ga	Cd	Zn
	Sb	Ca	Cu
	Sr	Al	Ag
$\leq 10^{-4}$	K	Mn(II)	Pb
	Cr(III)	Cs	

[a] Tracer metal concentrations in 1 *M* nitric acid extracted with a 5% solution of tri-*n*-octylphosphine oxide in toluene.

Table 5. Stripping agents for various elements

Element	Stripping agent
titanium	0.2 M sodium fluoride
iron(III)	0.3 M sulfuric acid
zirconium	1 M hydrofluoric acid
molybdenum(VI)	2 M ammonium hydroxide
bismuth	7 M nitric acid
thorium	0.3 M sulfuric acid
uranium(VI)	0.3 M sulfuric acid
	0.2 M sodium carbonate

Table 6. Colorimetric reagents for nonaqueous determinations

Element	Reagent	References
titanium	thiocyanate	211, 212
chromium	diphenylcarbazide	213, 214
iron	1,10-phenanthroline	200
zirconium	alizarin	211
	pyrocatechol violet	211,215
molybdenum	thioglycolic acid	200
tin	pyrocatechol violet	200
thorium	alizarin	211
uranium	dibenzoylmethane	216, 217

Extraction studies have been reported for many elements. Table 7 gives references to some of those studies.

Table 7. References to extraction studies on TOPO (non-synergistic)

Substance extracted	Reference
iron	218
bismuth	211
titanium	211, 212
zirconium	207, 211, 215
thorium	205, 208, 211, 219
cerium	220, 221
molybdenum	211
vanadium	222
niobium	211
tantalum	211
technetium	210
americium	206, 223
chromium	209, 213, 214
plutonium	206, 214, 224, 225
uranium	211, 216, 217, 222, 226, 227
nitric acid	205, 206, 211

Tris(2-ethylhexyl)phosphine Oxide as a Solvent Extractant

Tris(2-ethylhexyl)phosphine oxide, (TEHPO), is a viscous liquid. Some of its physical properties are given in Table 8.

Table 8. Physical properties of tris(2-ethylhexyl)phosphine oxide

Boiling point	Density	Refractive index	Reference
165-200/12 mm	--	--	222
205-215/203 mm	$.880^{30}$	1.465^{25}	222
161-190/.3 mm	$.867^{20}$	1.465^{25}	222
212/5 mm	$.893^{20}$	1.457^{25}	222
180-200/2 mm	--	--	228
156-166/.2 mm	$.9248^{20/20}$	1.4593^{31}	211
--	--	1.4643^{20}	229

Most of the work done with TEHPO has been of a qualitative nature. This work has been summarized by Ross and White (8) and part of it is presented in Table 9. TEHPO was found to be a poorer but more selective extractant than TOPO. Blake *et al*. (230) showed that uranium could be 99.6% extracted using a 0.1 *M* solution of TEHPO in carbon tetrachloride. Heyn and Banerjee (228, 231) have developed a method for the separation of uranium from bismuth using TEHPO. Their method is based on the fact that from 7 *M* nitric acid bismuth is

Table 9. Extraction of metal nitrates by tris(2-ethylhexyl)phosphine oxide[a]

Complete extraction	Partial extraction	No extraction		
U(VI)	Sb(III)	Al(III)	Ga(III)	Sm(III)
	Cr(VI)	As(V)	Ge(IV)	Ag(I)
	Au(I)	Ba(II)	Ho(III)	Sr(I)
	Hf(IV)	Be(II)	In(III)	Tb(III)
	Hg(II)	B(III)	Fe(III)	Tm(III)
	Mo(VI)	Cd(II)	La(III)	Ti(IV)
	Th(IV)	Ca(II)	Pb(II)	V(IV)
	Sn(IV)	Ce(III)	Mg(II)	Yb(III)
	Zr(IV)	Co(II)	Nd(III)	Y(III)
		Cu(II)	Ni(II)	Zn(II)
		Dy(III)	Pd(II)	
		Er(III)	Pt(II)	
		Eu(III)	Pr(III)	
		Gd(III)	Ru(III)	

[a] Extraction of 10 mg/ml or less of metal by a 0.1M solution of tris(2-ethylhexyl)phosphine oxide in cyclohexane.

only 0.05% extracted while uranium is 99.4% extracted. In this way uranium can be separated from a 10,000-fold excess of bismuth. Ross and White (232) worked out a procedure for the determination of tin in lead-, zinc-, iron, and zirconium-base alloys. Tin is extracted from an acidic chloride-sulfate solution and determined in the organic phase using pyrocatechol violet.

Bis(di-n-hexylphosphinyl)methane as a Solvent Extractant

Bis(di-n-hexylphosphinyl)methane, HDPM, is a white amorphous solid melting at 33-35°C and boiling at 221°C/.2 mm (6). Its density is 0.951 g/ml at 25°C and it has a refractive index of $N_d^{25} = 1.4735$ (6). The most recent value for its solubility in water is ~ 36-40 mg/l at 25°C (202) although an earlier value of 15.4 mg/l was reported (6).

Unlike TBP, TOPO, and TEHPO, nonpolar diluents are not satisfactory with HDPM (5). Third phases appear in the extraction of uranium when solvents like cyclohexane, toluene, or benzene are used. To avoid the formation of a third phase, solvents such as chloroform, 1-nitropropane or 1,2-dichlorobenzene must be used. 1,2-Dichlorobenzene is usually used because of its density, stability, and low water solubility.

The extractability of some metal nitrates is shown in Table 10 (6). Mrochek et al. (5) have studied the extraction of acids and uranium(VI) nitrate by HDPM. Unlike TOPO, HDPM forms two complexes with uranium, $UO_2(NO_3)_2 \cdot HDPM$ and $UO_2(NO_3)_2 \cdot 2HDPM$. The latter is the more stable complex and the one found when the ligand is in excess as is the case in any practical extraction. O'Laughlin (233) has studied the use of HDPM in the separation of cations by reversed-phase partition chromatography. The results were compared with

Table 10. Extraction of metal nitrates by bis(di-n-hexylphosphinyl)methane (6)

Medium	Quantitatively extracted	Partially extracted	Not extracted
1 M HNO_3	gold(III)	mercury(II)	aluminum
	bismuth	iron(III)	calcium
	thorium	samarium	copper(II)
	uranium(VI)	yttrium	gallium
	zirconium	molybdenum(VI)	lead(II)
			magnesium
			nickel(II)
			vanadium(V)
			zinc

those obtained using TBP and TOPO.

Effects of Structure on the Extracting Power of Neutral Organophosphorus Compounds

The types of compounds to be considered are trialkyl phosphates, $(RO)_3P\rightarrow O$, dialkyl alkylphosphonates, $(RO)_2RP\rightarrow O$, alkyl dialkylphosphinates, $(RO)R_2P\rightarrow O$, and trialkylphosphine oxides, $R_3P\rightarrow O$. As extractants the neutral organophosphorus compounds are very similar in many respects to a large number of other oxygen-containing solvents. Among these are ethers, esters, ketones, and alcohols. They all extract elements such as uranium(VI), neptunium(VI), plutonium(VI), protactinium(V), thorium(IV), neptunium(IV), zirconium(IV), and cerium(IV). They also all extract acids.

Because metal ions are hydrated in aqueous solution, the organic molecule must compete effectively with the water molecule for a place in the solvation sphere of the ion in order for extraction to take place. Uranyl nitrate in aqueous solution is largely hexasolvated (234, 235). The number of water molecules displaced depends on the solvating power of the extractant. With tributyl phosphate all the water molecules are displaced and the extracted species is $UO_2(NO_3)_2 \cdot 2TBP$ (43, 44). Tributylphosphine oxide also forms an anhydrous disolvate with uranyl nitrate (44). In the case of nitrates the extractant must also compete with the nitrate ion for coordination with the uranyl ion (236).

The ease with which the water molecules can be displaced depends upon the electron donor capabilities of the extracting molecules. Of course, in the G. N. Lewis theory of acids and bases (237, 238), electron donor strength is synonymous with base strength. In the case of the phosphorus compounds of the type XYZP-O where X, Y, and Z are substituents, the relative degree of basicity can be estimated from the infrared spectrum of the compound. The phosphoryl absorption frequency is used as the measure of basicity. The extent of $p\pi$ - $d\pi$ back bonding between the phosphorus and the oxygen depends upon the electronegativities of the substituents. Withdrawal of electrons away from the phosphorus atom results in an increase in the positive charge on that atom. This increases the phosphorus-oxygen bond order and causes an increase in the phosphoryl stretching frequency. Electropositive groups, of course, give the opposite effect. Therefore, the more basic compounds have the lower phosphoryl stretching frequencies.

Several mathematical expressions have been developed which relate the stretching frequency or wavelength with the electronegativities of the substituents. One of these (239) has the form:

$$\lambda\ (\text{microns})_{P\rightarrow O} = \frac{39.96 - \Sigma X}{3.995}$$

The term X is called the "phosphoryl absorption shift constant" and is directly related to the electronegativities of the substituent groups. Another relationship (229) is expressed as:

$$\nu\ (\text{cm}^{-1})_{P\rightarrow O} = 1172 + 13.96\ \Sigma\ \sigma^* + 4.11\ \Sigma\ E_s$$

This relates the stretching frequency to Taft's polar substituent constant (σ^*) which is a measure of inductive effects and to his steric substituent constant (E_s). The second expression takes into account steric factors while the first one does not and is said, therefore, to give a much better correlation between experimental and calculated frequencies.

The correlation between base strength and extracting ability has been confirmed in some cases. In general the following orders of base strength and extracting ability hold: trialkylphosphine oxides > alkyl dialkylphosphinates >

dialkyl alkylphosphonates > trialkyl phosphates (2, 3, 240-242). However, within a given class of compounds there does not seem to be an exact correlation between phosphoryl stretching frequency and distribution coefficient.

Electronegative groups such as chlorine, phenoxy, phenyl, alkoxy, allyl, or noncomplexing phosphoryl reduce distribution coefficients. Tribenzyl phosphate appears to be somewhat anomalous in that it is a relatively poor extractant, while benzyl amine is a relatively strong base (35). It may be that the benzyl group in tribenzyl phosphate favors a large amount of phosphorus-oxygen double bonding because this would give a conjugated system with resonance stabilization. Triphenylphosphine oxide is a poor extractant; however, it forms an extremely thermally stable crystalline complex with uranyl nitrate (MP 289-293°C) (3). Presumably the lattice energy is greater than the heat of solvation by the inert solvents used to dilute the extractant. Among the phosphates the low distribution coefficients obtained with the diphosphoryl reagents show that the non-complexing phosphoryl (with uranyl nitrate the ligand:metal ratio is 2:1, leaving two free phosphoryl groups in the complex if the diphosphoryl ligands are monodentate) functions as an electron withdrawing substituent on the adjacent complexing phosphoryl group (240). Increasing the length of the carbon bridge between the phosphorus atoms decreases this effect (240).

Table 11. Effects of electronegative substituents on the extraction of uranium(VI) nitrate by organophosphorus reagents

Reagent	Distribution coefficient	
tri-n-butyl phosphate	0.19[a]	0.25[b]
di-n-butyl allylphosphate	0.14[a]	
di-n-butyl ethoxybutylphosphate	0.14[a]	
di-n-butyl phenylphosphate		0.0035[b]
tri-n-butyl phosphate	0.19[a]	0.25[b]
tri-n-butoxyethyl phosphate	0.14[a]	
triallyl phosphate		0.018[b]
triphenyl phosphate	0.01[a]	0.00067[b]
tris(2-chloroethyl) phosphate	0.01[a]	
di-n-butyl n-butylphosphonate	24.00[c]	
bis(di-n-butoxyphosphinyl)ethane		5.7[b]
bis(di-n-butoxyphosphinyl)methane	12.55[c]	1.0[b]
diethyl n-hexylphosphonate	1.02[a]	
diethyl phenylphosphonate	0.30[a]	
diethyl benzoylphosphonate	0.018[a]	

---

[a] 0.5 M ligand in carbon tetrachloride, 0.2 M uranium(VI) nitrate (3).

[b] 0.19 M ligand in benzene, 8 x 10^{-4} M uranium(VI) nitrate, 0.5 M nitric acid (78).

[c] 0.5 M ligand in carbon tetrachloride, 50 g/l uranium, 1 M nitric acid, phase ratio organic:aqueous is two (243).

Table 11. (Continued)

Reagent	Distribution coefficient	
tri-n-octylphosphine oxide	310[d]	
tri-γ-phenyl-n-propylphosphine oxide	85[d]	15[e]
tri-β-phenylethylphosphine oxide		10[e]

[d] 0.1 M ligand in carbon tetrachloride, 0.004 M uranium(VI) nitrate, 0.1 M nitric acid, phase ratio organic:aqueous is two (222).

[e] 0.05 M ligand in carbon tetrachloride, 0.004 M uranium(VI) nitrate, 0.1 M nitric acid, phase ratio organic: aqueous is two (222).

Strongly electronegative groups such as chlorine atoms seem to have a greater effect in depressing the extraction coefficient than the phosphoryl frequency shift would predict (3). It may be that the phosphoryl frequency is not an exact measure of basicity. In some cases, where the phosphoryl band appears as a doublet, it has been suggested that there is an interaction of phosphoryl groups with one another or with substituents (229). These same factors may affect the frequency at which a singlet appears. It was previously noted that for the best correlation between experimental and calculated phosphoryl frequencies it is necessary to take into consideration steric factors. It would not be too surprising if the steric factors involved in the coordination of a ligand with a metal atom were much greater than those which affect the phosphoryl frequency of the ligand.

All the neutral organophosphorus compounds are capable of extracting acids. However, only a few of them are strong enough bases to be titrated. Several attempts to titrate phosphine oxides in nonaqueous media have failed. However, the titration of trimethylphosphine oxide, tri-n-octyphosphine oxide, and triphenylphosphine oxide has been reported recently (244). Acetic anhydride was used as the solvent with perchloric acid in dioxane as the titrant. A modified calomel and glass electrode system was used. There is no simple connection between bonding to a metal and bonding to an acid although as a rough approximation there is a correlation (35). Metal ions being much larger than protons are more susceptible to steric considerations.

To obtain the maximum phosphoryl basicity all the substituent groups must be electropositive, e.g., alkyl groups. That this is so is clearly seen in the increased basicity and greater distribution coefficients in the series phosphine oxide > phosphinate > phosphonate > phosphate (see Table 12) where alkyl groups have replaced alkoxy groups in stepwise fashion. Increasing the chain length increases the electropositive character of the alkyl group and, therefore, should increase the distribution coefficient. However, the effect becomes negligible after the chain reaches about four carbon atoms in length. A second way to increase the electropositive character of the alkyl groups is to have a branched chain.

Table 12. Effects of the number of P-C bonds on the extraction of uranium by organophosphorus reagents

Reagent	Distribution coefficient	
tri-n-butyl phosphate	0.19[a]	0.25[b]
di-n-butyl n-butylphosphonate	1.03[a]	10.0[b]
n-butyl di-n-butylphosphinate	3.9[a]	120[b]
tri-n-butylphosphine oxide	23.0[a]	380[b]

[a] 0.5 M ligand in carbon tetrachloride, 0.2 M uranium(VI) nitrate (3).

[b] 0.19 M ligand in benzene, 8 x 10^{-4} M uranium(VI) nitrate, 0.5 M nitric acid (78).

The t-butyl group is significantly more electropositive than the sec-butyl group which, in turn, is more electropositive than the n-butyl group. However, the iso-butyl group is approximately equivalent to the n-butyl group, which would seem to indicate that to be effective the branching must be next to the point of attachment of the group. There is not enough evidence to be certain about this. The cyclohexyl group is not as electropositive as the n-hexyl group and the former would not be expected to be as effective substituent as the latter but there are no comparative data. The cyclopentyl group is more electropositive than the cyclohexyl group.

The steric availability of the electrons at the oxygen atom must be considered as well as the electron density. It will be of little use to have highly electropositive groups if at the same time they provide great steric hindrance. Table 18, which gives a list of Taft's steric substituent constants (245) of a number of groups, enables one to compare the relative steric effects of various groups. For the normal groups, increasing the chain length does not increase the steric hindrance. Branching, on the other hand, greatly increases the steric effect.

Table 13. Effects of alkyl chain length on the extraction of uranium(VI) nitrate by organophosphorus reagents

Reagent	Distribution coefficient	
di-*n*-butyl *n*-decylphosphonate	1.10[a]	
di-*n*-butyl *n*-hexylphosphonate	1.05[a]	
di-*n*-butyl *n*-amylphosphonate		25.75[b]
di-*n*-butyl *n*-butylphosphonate	1.03[a]	24.00[b]
di-*n*-butyl *n*-propylphosphonate		22.20[b]
di-*n*-butyl ethylphosphonate	0.96[a]	13.05[b]
di-*n*-butyl methylphosphonate		10.35[b]
di-*n*-decyl methylphosphonate	14.65[b]	
di-*n*-nonyl methylphosphonate	32.60[b]	

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[a] 0.5 *M* ligand in carbon tetrachloride, 0.2 *M* uranium(VI) nitrate (3).

[b] 0.5 *M* ligand in carbon tetrachloride, 50 g/l uranium, phase ratio organic:aqueous is two (243).

Table 13. (Continued)

Reagent	Distribution coefficient	
di-*n*-octyl methylphosphonate	50.70[b]	
di-*n*-heptyl methylphosphonate	107.1[b]	
di-*n*-hexyl methylphosphonate	18.45[b]	
di-*n*-butyl methylphosphonate	10.35[b]	
diisoamyl *n*-octylphosphonate	11.50[b]	
diisoamyl *n*-amylphosphonate	28.40[b]	
diisoamyl *n*-propylphosphonate	22.30[b]	
diisoamyl methylphosphonate	21.10[b]	
tri-*n*-octyl phosphate	8.5[c]	33[d]
tri-*n*-hexyl phosphate		38[d]
tri-*n*-amyl phosphate		32[d]
tri-*n*-butyl phosphate	3.1[c]	26[d]
tri-*n*-propyl phosphate	1.4[c]	
di-*n*-butyl *n*-decylphosphate	0.17[a]	
di-*n*-butyl *n*-octylphosphate	0.19[a]	
di-*n*-butyl *n*-hexylphosphate	0.21[a]	
tri-*n*-butyl phosphate	0.19[a]	

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[c] 0.732 *M* ligand in carbon tetrachloride, 0.01 *M* uranium(VI) nitrate, 0.1 *M* nitric acid (246).

[d] 1.09 *M* ligand in *n*-dodecane, tracer amounts of uranium, 3 *M* nitric acid (7).

Table 13. (Continued)

Reagent	Distribution coefficient	
di-*n*-butyl ethylphosphate	0.15[a]	
di-*n*-butyl methylphosphate	0.14[a]	
diethyl *n*-decylphosphate	0.11[a]	
diethyl *n*-amylphosphate	0.17[a]	
diethyl *n*-butylphosphate	0.17[a]	9.7[c]
triethyl phosphate		1.7[c]
n-butyl di-*n*-butylphosphinate	3.9[a]	
n-propyl di-*n*-butylphosphinate	3.2[a]	
methyl di-*n*-butylphosphinate	3.8[a]	
tri-*n*-decylphosphine oxide	280[e]	
tri-*n*-octylphosphine oxide	330[e]	
tri-*n*-butylphosphine oxide	80[e]	

[e] 0.1 *M* ligand in carbon tetrachloride, 0.004 *M* uranium(VI) nitrate, 0.1 *M* nitric acid, phase ratio organic:aqueous is two (222).

Table 14. Effects of alkyl chain length on the extraction of thorium nitrate by organophosphorus reagents

Reagent	Distribution coefficient[a]
tri-*n*-butyl phosphate	2.9
tri-*n*-amyl phosphate	2.9
tri-*n*-hexyl phosphate	3.0
tri-*n*-octyl phosphate	2.4

[a] 1.09 M ligand in *n*-dodecane, tracer metal concentration, 3 M nitric acid (7).

Table 15. Effects of alkyl chain branching on the extraction of uranium(VI) nitrate by organophosphorus reagents

Reagent	Distribution coefficient		
triisobutyl phosphate	0.25[a]	22[b]	3.0[c]
tri-*n*-butyl phosphate	0.25[a]	26[b]	3.1[c]
tri-*sec*-butyl phosphate	0.54[a]	42[b]	15.1[c]
tri-*n*-octyl phosphate	33[b]	8.5[c]	
tris(2-ethylhexyl) phosphate	58[b]	9.0[c]	
triisoamyl phosphate	34[b]		9.0[c]
tri-*n*-amyl phosphate	32[b]		

[a] 0.19 M ligand in benzene, 8 x 10^{-4} M uranium(VI) nitrate, 0.5 M nitric acid (78).

[b] 1.09 M ligand in *n*-dodecane, tracer amounts of uranium, 3.0 M nitric acid (7).

[c] 0.732 M ligand in carbon tetrachloride, 0.01 M uranium(VI) nitrate, 1.0 M nitric acid (246).

Table 15. (Continued)

Reagent	Distribution coefficient
tris(3-amyl) phosphate	49[b]
tri-_n_-hexyl phosphate	38[b]
tricyclohexyl phosphate	133[c]
tri-_n_-octylphosphine oxide	310[d]
tris(2-ethylhexyl)phosphine oxide	8[d]
tri-_n_-decylphosphine oxide	280[d]
tris(3,5,5-trimethylhexyl)-phosphine oxide	330[d]
di-_n_-hexyl methylphosphonate	18.45[e]
dicyclohexyl methylphosphonate	44.10[e]
di-_n_-butyl ethylphosphonate	13.05[e]
diisobutyl ethylphosphonate	22.50[e]
diisoamyl _n_-amylphosphonate	21.10[e]
diisoamyl isoamylphosphonate	28.40[e]

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[d] 0.10 _M_ ligand in carbon tetrachloride, 0.004 _M_ uranium(VI) nitrate, 0.10 _M_ nitric acid, phase ratio aqueous: organic is two (222).

[e] 0.5 _M_ ligand in CCl_4, 50 g/l uranium, 1 _M_ nitric acid, phase ratio organic:aqueous is two (243).

Table 16. Effects of alkyl chain branching on the extraction of thorium nitrate by organophosphorus reagents

Reagent	Distribution coefficient[a]
triisoamyl phosphate	4.2
tri-*n*-amylphosphate	2.9
tris(3-amyl) phosphate	0.22
tris(3-methyl-2-butyl) phosphate	0.18
tris(4-methyl-2-amyl) phosphate	0.047

[a] 1.09 *M* ligand in *n*-dodecane, tracer amounts of thorium, 3.0 *M* nitric acid (7).

Table 17. Taft polar substituent constants (σ^*) (245)

Group	σ^*	Group	σ^*
Cl_3C	+2.65	$ClCH_2$	+1.050
F_2CH	2.05	$BrCH_2$	1.000
CH_3O_2C	2.00	ICH_2	0.85
Cl_2CH	1.94	CF_3CH_2	0.02
$(CH_3)_3N^+CH_2$	1.90	$C_6H_5OCH_2$	0.85
CH_3CO	1.65	$C_6H_5(OH)CH$	0.765
$C_6H_5C{\equiv}C$	1.35	CH_3COCH_3	0.60
$CH_3SO_2CH_2$	1.32	C_6H_5	0.600
$CNCH_2$	1.300	$HOCH_2$	0.555
FCH_2	1.10	CH_3OCH_2	0.520
HO_2CCH_2	+1.05	$NO_2(CH_2)_2$	+0.50

Table 17. (Continued)

Group	σ*	Group	σ*
H	+0.490	cyclo-$C_6H_5CH_2$	-0.06
$C_6H_5CH{=}CH$	0.410	C_2H_5	0.100
$(C_6H_5)_2CH$	+0.405	$\underline{n}$-C_3H_7	0.115
$Cl(CH_2)_2$	+0.385	$\underline{i}$-C_4H_9	0.125
$CH_3CH{=}CH$	0.360	$\underline{n}$-C_4H_9	0.130
$CF_3(CH_2)_2$	0.32	cyclo-C_6H_{11}	0.15
$C_6H_5CH_2$	0.215	$\underline{t}$-$C_4H_9CH_2$	0.165
$CH_3CH{=}CHCH_2$	0.13	$\underline{i}$-C_3H_7	0.190
$CF_3(CH_2)_3$	0.12	cyclo-C_5H_7	0.20
$C_6H_5(CH_3)CH$	0.11	$\underline{s}$-C_4H_9	0.210
$C_6H_5(CH_2)_2$	0.080	$(C_2H_5)_2CH$	0.225
$C_6H_5(C_2H_5)CH$	0.04	$(CH_3)_3SiCH_2$	0.26
$C_6H_5(CH_2)_3$	+0.02	$(\underline{t}$-$C_4H_9)(CH_3)CH$	0.28
CH_3	0.000	$\underline{t}$-C_4H_9	-0.300

Table 18. Taft steric substituent constants (E_s) (245)

Group	E_s	Group	E_s
$H(C_6H_5)$	+1.24	F_2CH	-0.67
CH_3	0.00	$\underline{c}$-C_6H_{11}	0.79
C_2H_5	-0.07	$CH_3OCH_2CH_2$	-0.77
$\underline{c}$-C_4H_7	0.06	$\underline{i}$-C_4H_9	0.93
CH_3OCH_2	0.19	$\underline{c}$-$C_6H_{11}CH_2$	0.98
$ClCH_2$,FCH_2	0.24	$(CH_3)(C_2H_5)CH$	1.13
$BrCH_2$	0.27	F_3C	1.16
CH_3SCH_2	0.34	$\underline{c}$-C_7H_{13}	1.10
ICH_2	0.37	$(CH_3)(C_6H_5)CH$	1.19
$\underline{n}$-C_3H_7	0.36	$\underline{t}$-C_4H_9	1.54
$\underline{n}$-C_4H_9	0.39	$(C_6H_5)(C_2H_5)CH$	1.50
$\underline{n}$-C_5H_{11}	0.40	Cl_2CH	1.54
$\underline{i}$-C_5H_{11}	0.35	$\underline{t}$-$C_4H_9CH_2$	1.74
$\underline{n}$-C_8H_{17}	0.33	$(C_6H_5)_2CH$	1.76
$\underline{t}$-$C_4H_9CH_2CH_2$	0.34	(CH_3)(neopentyl)CH	1.85
$C_6H_5OCH_2$	0.33	Br_2CH	1.86
$C_6H_5CH_2$	0.38	$(C_2H_5)_2CH$	1.98
$C_6H_5(CH_2)_2$	0.38	Cl_3C	2.06
$C_6H_5(CH_2)_3$	0.45	$(\underline{n}$-$C_3H_7)_2CH$	2.11
$\underline{i}$-C_3H_7	0.47	$(\underline{i}$-$C_4H_9)_2CH$	2.47
$\underline{c}$-C_5H_9	-0.51	$(Br)_3C$	-2.43

Table 18. (Continued)

Group	E_s	Group	E_s
$(CH_3)_2$(neopentyl)C	-2.57	$(CH_3)_2(\underline{t}\text{-}C_4H_9)C$	-3.9
$(\text{neopentyl})_2CH$	3.18	$(C_2H_5)_3C$	3.8
$(CH_3)(\underline{t}\text{-}C_4H_9)CH$	-3.33	$(CH_3)(\underline{t}\text{-}C_4H_9)$(neopentyl)	-4.0

Bulky groups or branched-chains can physically hinder the approach of the extractant molecule to the coordination sphere of the metal ion as well as have a great effect on the basicity of the extractant molecule (247). As expected from the electron donating ability of alkyl groups, methylamine is a considerably stronger base than ammonia. Dimethylamine, however, is only slightly stronger than methylamine, and trimethylamine is considerably weaker even though it should have the nitrogen of greatest electron density of the compounds just mentioned. This phenomenon has been explained in two ways. One theory is that when the amine accepts a proton there is a compression of the alkyl groups on the back side of the molecule away from the added proton. Because this is in opposition to their repulsive forces, strain is produced. This strain is called back strain. This same theory has been used to explain why ethers are weaker bases than alcohols and why water is a stronger base than methanol or ethanol. The second theory proposed to explain the weakly basic character of trimethylamine deals with the ease of solvation of the protonated species. This theory says that decreasing the number of hydrogen atoms by increasing the number of alkyl groups makes it more difficult to solvate the protonated species because in aqueous solution the solvation is accomplished by hydrogen bonding to water molecules. In support of this theory is the fact that tri-n-butylamine is a stronger base than mono- or di-n-butylamine in chlorobenzene solution.

It has been inferred from entropy calculations that in the case of phosphates and phosphonates complex alkyl groups do not sterically hinder the extraction of uranium (35). Likewise, in the extraction of zirconium with phosphates, branching in the carbon chain increases rather than decreases extraction (248). However, the extraction of thorium nitrate by phosphates is greatly depressed when bulky alkyl groups are introduced into the extractant molecule (7). In this case thorium may require three extractant molecules while only two are required for the other actinides. Evidence has been presented both for thorium nitrate requiring two extractant molecules (66) and for requiring three extractant molecules (67, 141). Steric factors are more apparent in the phosphine oxides than in the phosphates because the phosphine oxides do not have oxygen atoms separating the alkyl groups from the phosphoryl group. The poor extraction properties of tris(2-ethylhexyl)phosphine oxide is attributed to steric hindrance

(222).

The size and type of alkyl substituents help determine the solubility of the complex in the inert, organic solvent. Varying them should change that solubility and affect the extraction properties. However, it may be that this change is overshadowed by steric and basicity factors. At least in the case of the extraction of uranium by phosphates and phosphonates it has been said that no evidence could be found for solubility effects (3). The relatively low distribution coefficient of tributylphosphine oxide for uranium has been explained as being caused by the solubility of the complex in water (222).

In some cases, polymers are formed when the extracted metal reaches a certain concentration. One to one ratios of metal to ligand with diphosphonates may indicate chelates or polymers (78). There is also evidence of polymerization in the extraction of uranium with di(2-ethylhexyl) phosphate (249) and dibutyl phosphate (3, 250). Polymerization, of course, tends to reduce the activity of the extractable species in the organic phase (251). This shifts the overall extraction equilibrium in favor of higher distribution ratios.

INVESTIGATIONS

Experimental

Solvents

Reagent-grade solvents were used except for 1,2-dichlorobenzene which had a stated purity of 99+%. The 1,2-dichlorobenzene was purified by passing it through a column packed with basic alumina. When bis(di-n-alkylphosphinyl)methanes are used as extractants, nonpolar diluents such as carbon tetrachloride and cyclohexane are not capable of dissolving the metal-ligand complexes and third phases are formed. With vigorous shaking, carbon tetrachloride will form a suspension of the uranium(VI) nitrate-ligand complex that is stable for several days. Diluents that can form hydrogen bonds with the phosphoryl groups should also be avoided if possible. In this respect 1,2-dichlorobenzene was found to be superior to chloroform, cyclohexanol, or n-hexanol as a diluent in the extraction of uranium(VI) nitrate and thorium nitrate. 1,2-Dichlorobenzene was usually used as the diluent because of its good stability, appropriate density, lack of water solubility, lack of acidic protons, and its fairly high dielectric constant. However, it was not suitable for infrared studies of the metal-ligand complexes because of its strong absorption bands. Therefore, 1,2-dichloroethane was used for infrared studies. The best diluents for trialkylphosphine oxides are nonpolar solvents such as cyclohexane and carbon tetrachloride.

These solvents were used whenever possible.

Inorganic reagents

All inorganic reagents used were reagent-grade or better. Primary standard potassium nitrate was used for maintaining ionic strength. Standard uranium(VI) nitrate and samarium nitrate solutions were prepared by dissolving the oxides in nitric acid. Thorium nitrate solutions were prepared by dissolving thorium nitrate pentahydrate in water. The thorium nitrate had been analyzed by ignition to the oxide and found to contain 40.67% thorium.

Extractions

The general procedure for extractions was to take 10 ml each of the aqueous and organic solutions and to equilibrate them for ten to fifteen minutes. The extractions were performed with 60-ml glass separatory funnels fitted with Teflon stopcock plugs. Equilibrations were done using a Burrell "wrist action" shaker. All extractions were performed at room temperature, ~ 25°C. After equilibration, complete phase separation was insured by using an International Model CL Centrifuge.

Inorganic analyses

Uranium was determined in the aqueous phase using arsenazo (252), peroxide (253), or the visible spectrum of uranium(VI) nitrate (253). Uranium in the organic phase was determined by first stripping with a solution of sodium carbonate followed by the use of peroxide. Thorium was determined in the aqueous phase with thorin (254) or by arsenazo III (255). Thorium in the organic phase was determined using thorin in 95% ethanol. In this method an aliquot of the organic phase is diluted with 50 ml of 95% ethanol, 10 ml of a 0.1% aqueous thorin solution is added, and the pH is adjusted to 0.8. A final dilution to 100 ml is made with 95% ethanol. A similar method has been published in which butyl cellosolve is used instead of ethanol (256). Whenever the method using thorin is applied, the acid used for pH adjustment should be the same as the one used to fix the extraction conditions. The same acid must be used in preparing the calibration curve. Samarium was analyzed for by titration of the aqueous phase with ethylenediamine tetraacetic acid (EDTA) using brompyrogallol red as an indicator (257). The titrations were performed using a Sargent-Malmstadt automatic spectro/electro titrator. Nitric acid was stripped from the organic phase with water and titrated with sodium hydroxide. Alternatively the nitric acid was determined in the organic phase by titration with tetrabutylammonium hydroxide using _t_-butyl alcohol as a solvent and thymolphthalein as an indicator. A Beckman Model G pH meter was used for all pH measurements. It was calibrated using Beckman standard buffers.

Extractants

Bis(di-n-hexylphosphinyl)methane, HDPM, and bis(dicyclohexylphosphinyl)methane were secured from Ames Laboratory stock. Bis(di-2-ethylbutylphosphinyl)methane, EBDPM, and bis(di-2-ethylhexylphosphinyl)methane, EHDPM, were synthesized using the general procedure given by Richard et al. (4) for the synthesis of bis(dialkylphosphinyl)methanes. Tri-n-octylphosphine oxide, TOPO, an Eastman white-label product, and purified tri-n-butyl phosphate, TBP, were purchased. Tris(2-ethylhexyl)phosphine oxide, TEHPO, was synthesized according to the procedure of Heyn and Banerjee (228) or was purchased from Chemicals Procurement Laboratories, Inc., College Point 56, New York. Acidic impurities were removed from the extractants by treatment with aqueous sodium hydroxide.

Synthesis of EHDPM

The preparation of EHDPM has not been previously reported. It was prepared according to the general procedure of Richard et al. (4). Bis(dichlorophosphinyl)methane in hot, anhydrous benzene was caused to react with a fourfold excess of 2-ethylhexylmagnesium bromide dissolved in ether. The solution was worked up in the usual manner and the organic material distilled. The products from three distillation fractions were identified as follows:

(a) di-2-ethylhexylmethylphosphine oxide: B.P. 170-195/2.5 mm; %P calc. for $C_{17}H_{37}PO$=10.74, %P found = 10.2;

infrared spectrum shows P-CH_3 stretching frequencies at 1290 cm^{-1} and 889 cm^{-1}. This compound is not reported in the literature. The yield was not measured.

(b) tris(2-ethylhexyl)phosphine oxide: B.P. 207-215/ 1.5 mm; N_D^{25} = 1.4654; %P calculated for $C_{25}H_{51}PO$ = 8.01, %P found = 8.04. Heyn and Banerjee (228) give the B.P. as 180-200°/2 mm. Blake <u>et al</u>. (222) give the B.P. as 200-215°/2-3 mm and N_D^{25} as 1.465. The yield was not measured.

(c) bis(di-2-ethylhexylphosphinyl)methane: B.P. 239-251°/1 mm; calculated for $C_{33}H_{70}P_2O_2$, %C = 70.67, %H = 12.58, %P = 11.04; found, %C = 70.3, %H = 12.4, %P = 10.8. The yield was ~ 15-30% based on the amount of bis(dichlorophosphinyl)-methane used.

A preliminary examination of the properties of EHDPM as an extractant did not reveal any exceptional properties. Uranium(VI), thorium, tin(IV), and chromium(VI) are extracted well from hydrochloric acid. Vanadium(V) and molybdenum(VI) are extracted well only at high hydrochloric acid concentrations while magnesium, copper, palladium, indium, zinc, cobalt, nickel, and iron(III) are poorly extracted. Uranium(VI) and thorium can be quantitatively extracted from nitric acid solutions while aluminum, bismuth, copper, nickel, iron(III), silver, indium, zinc, magnesium, cobalt, and samarium are poorly extracted. Uranium(VI) perchlorate can be extracted by EHDPM but not nearly as well as the nitrate or chloride.

Organic analyses

The method of Lysyj and Zarembo (258) was used for the carbon-hydrogen analyses. Phosphorus was determined as the phosphomolybdivanado complex (259) subsequent to oxidation in a Schöniger flask. A remote ignition unit (F and M model 141) was used in connection with the Schöniger flask.

Spectra

Ultraviolet and visible spectra were scanned using a Cary model 14 recording spectrophotometer. Spectrophotometric analyses were made with the Beckman model DU spectrophotometer. Infrared spectra were obtained using a Beckman IR-7 instrument which was calibrated using atmospheric carbon dioxide and air. It is accurate to ± 2 cm^{-1}. Infrared spectra of metal complexes in solution were obtained using Eastman Kodak Irtran II (ZnS) cell windows. The Irtran II windows were rubbed with ground glass to eliminate the appearance of interference fringes. For other than the metal complexes, sodium chloride or potassium bromide cell windows were used. Nuclear magnetic resonance spectra were obtained using a Varian associates model HR-60 high resolution instrument.

Basicity of the Phosphoryl Group

The basicity of the phosphoryl group was examined from several points of view. Information was desired on the extent of the basicity of the phosphoryl group, whether or not it could be titrated, and on the relative basicities of the phosphoryl compounds used as extractants.

Fritz (260) has shown that the use of nonaqueous solvents allows many organic acids and bases to be titrated which are weaker than water. Blake, Brown, and Coleman (222) stated that they were unable to titrate phosphine oxides as weak bases in acetic acid or in chloroform. The titrant used was not given. Gremillion (261) successfully used acetic anhydride as a solvent and perchloric acid in glacial acetic acid as a titrant for the determination of very weak bases such as pyridine and ureas. Wimer (244) has reported the titration of trimethylphosphine oxide, trioctylphosphine oxide, and triphenylphosphine oxide. He used perchloric acid in dioxane as the titrant and acetic anhydride as the solvent. The titrations were done potentiometrically.

The general applicability of Wimer's work to a number of different phosphoryl-containing compounds was tested. The titrant was prepared by dissolving 9 ml of 70% perchloric acid in glacial acetic acid, adding 25 ml of acetic anhydride, and diluting to one liter with glacial acetic acid. The solution was allowed to stand 24 hours prior to use so that the acetic anhydride would have time to remove all the water present. In some cases dioxane was used as the diluent instead of glacial acetic acid. Reagent-grade dioxane was further purified and dried by first refluxing with sodium and then distilling. When dioxane was used as the diluent no acetic anhydride was added. The titrant was standardized potentiometrically against primary standard potassium acid phthalate dissolved in glacial acetic acid.

The titrations were carried out using a Beckman Model G pH meter with calomel and glass electrodes. To minimize liquid junction potentials, the aqueous bridge in a sleeve-type calomel electrode was replaced with a saturated solution of anhydrous lithium perchlorate in acetic anhydride. A fiber-type calomel electrode with an aqueous salt bridge can be used but the potential readings are somewhat unstable. An attempt was made to replace the calomel electrode with a silver-silver chloride electrode, but the silver-silver chloride electrode did not respond properly. The chloride ions were probably reacting with the titrant. Samples of 0.5 to 2 millimoles were dissolved in 100 ml of acetic anhydride, stirred with a magnetic stirrer, and titrated with 0.1 N perchloric acid in acetic acid.

Three basic types of phosphoryl compounds were titrated: trialkylphosphine oxides, bis(dialkylphosphinyl)alkanes, and β-ketophosphine oxides. The results for these and other compounds are reported in Table 19. Compounds in which the phosphoryl group was surrounded by either highly electronegative groups (e.g. triphenylphosphine oxide) or by very bulky groups (e.g. tris(2-ethylhexyl)phosphine oxide) gave poorly defined end-points. Very weakly basic compounds such as di-n-octylphosphine oxide and di-n-butyl n-butylphosphonate

Table 19. Titration of phosphoryl compounds[a]

Compound	% Purity	
tri-*n*-octylphosphine oxide	99.8	100.0
tris(2-ethylhexyl)phosphine oxide	—[b]	
di-2-ethylhexylmethylphosphine oxide	83.3	
triphenylphosphine oxide	—[b]	
di-*n*-octylphosphine oxide	—[c]	
di-*n*-butyl *n*-butylphosphonate	—[c]	
di-*n*-heptylphosphinic acid	—[c]	
bis(di-*n*-hexylphosphinyl)methane	100.6	100.5
bis(dicyclohexylphosphinyl)methane	97.6	98.2
bis(di-2-ethylbutylphosphinyl)methane	99.3	
bis(di-2-ethylhexylphosphinyl)methane	—[b]	
[(di-*n*-octylphosphinyl)(diphenylphosphinyl)]methane	102.4	102.7
bis(di-*n*-hexylphosphinyl)ethane	100.5	101.1
bis(di-*n*-hexylphosphinyl)propane	99.6	100.4
bis(di-*n*-hexylphosphinyl)butane	100.2	99.8
acetonyldi-*n*-hexylphosphine oxide	102.2	101.8
phenacyldi-*n*-hexylphosphine oxide	97.6	97.7
phenacyldiphenylphosphine oxide	—[b]	

[a] Titrant--perchloric acid in acetic acid.

[b] Poorly defined end-point.

[c] Not titratable.

could not be titrated at all.

Bis(di-*n*-hexylphosphinyl)methane and bis(di-*n*-hexylphosphinyl)ethane each have one titratable phosphoryl group. However, bis(di-*n*-hexylphosphinyl)propane and bis(di-*n*-hexylphosphinyl)butane are diacidic bases.

The potential breaks obtained at the end-points are given in Table 20. As can be seen, the magnitude of the potential break is dependent upon the volume of titrant used. In the acetic anhydride solution the acid which acts as the titrant is acetyl perchlorate. Increasing the acetic acid concentration causes the formation of species less acidic than acetyl perchlorate and results in poorer end-points. Perchloric acid in acetic anhydride gradually decomposes giving rise to a yellow solution. However, this decomposition is slow enough to permit accurate determinations to be made. Thus, at least in certain cases, the phosphoryl group is basic enough to be titrated. This affords a rapid and convenient method for quantitative determinations to be made.

A number of workers have reported a correlation between the phosphoryl stretching frequency and the electronegativity of substituent groups. This implies that the bond order varies and with it the force constant of the phosphoryl bond. Compounds such as triphenylphosphine oxide and trichlorophosphine oxide where the phosphoryl group has largely double bond character have relatively high phosphoryl stretching frequencies. Trialkylphosphine oxides have more single bond

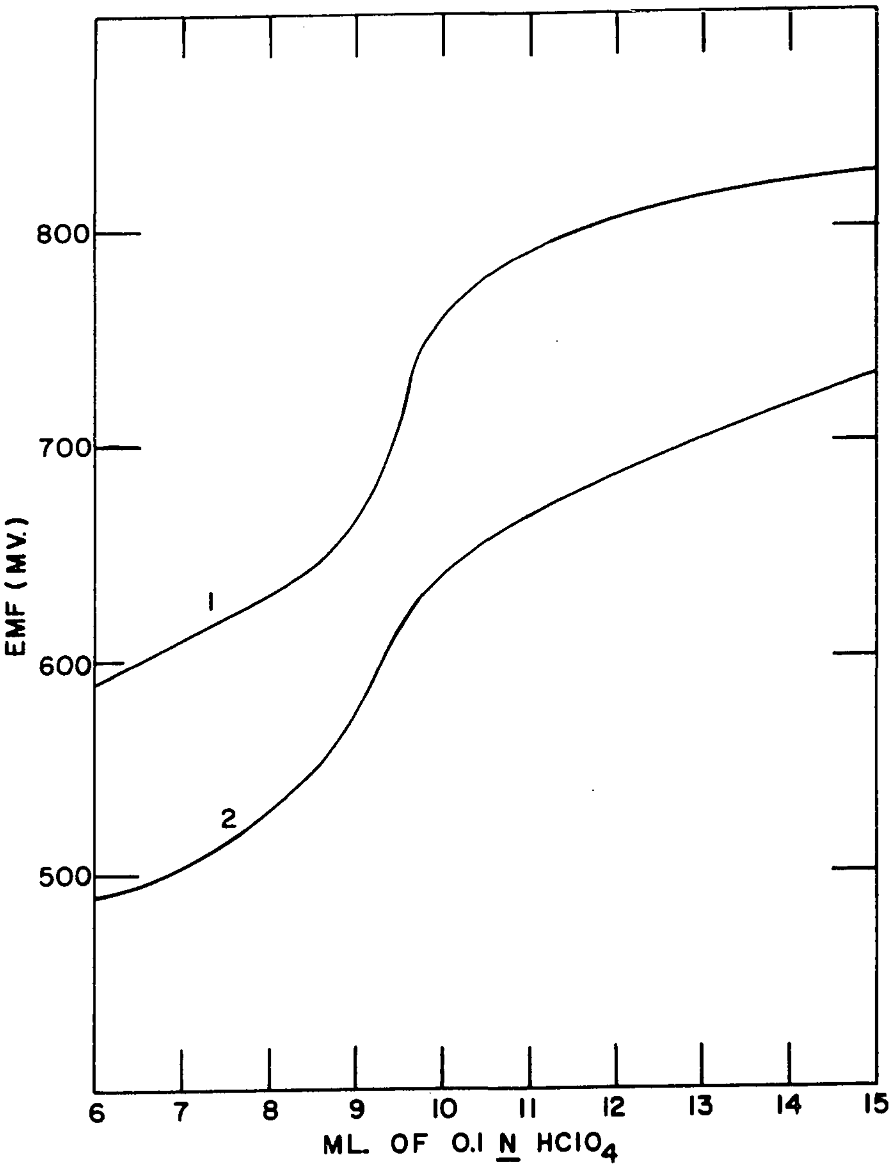
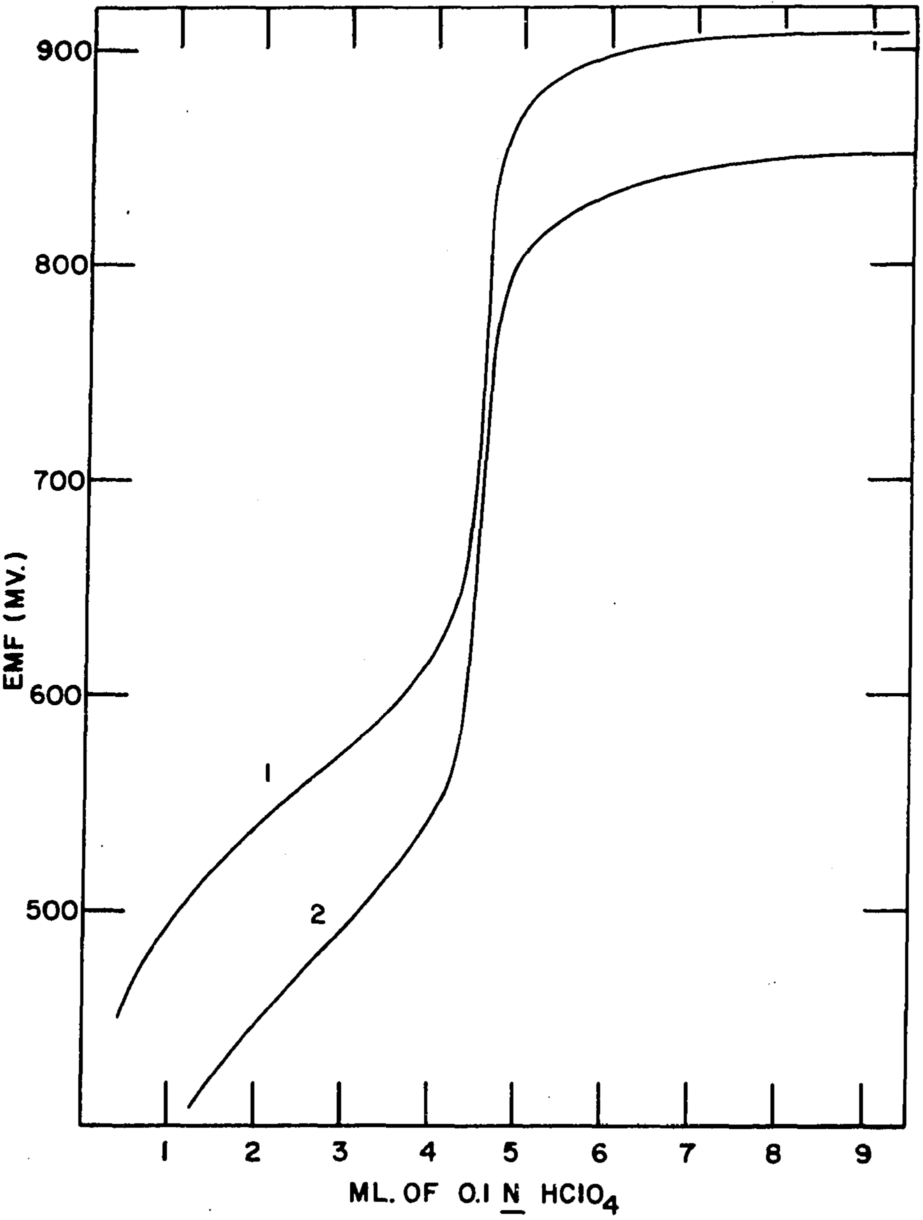


Figure 1. Titration of bis(di-alkylphosphinyl)alkanes

1. Bis(di-n-hexylphosphinyl)methane
2. Bis(di-n-hexylphosphinyl)ethane

Figure 2. Titration of tri-_n_-octylphosphine oxide using (1) a glass electrode and a calomel electrode with an aqueous bridge and (2) a glass electrode and a calomel electrode with a nonaqueous bridge


900
800
700
600
500
EMF (MV.)
1
2
1
2
3
4
5
6
7
8
9
ML. OF 0.1 N HClO4

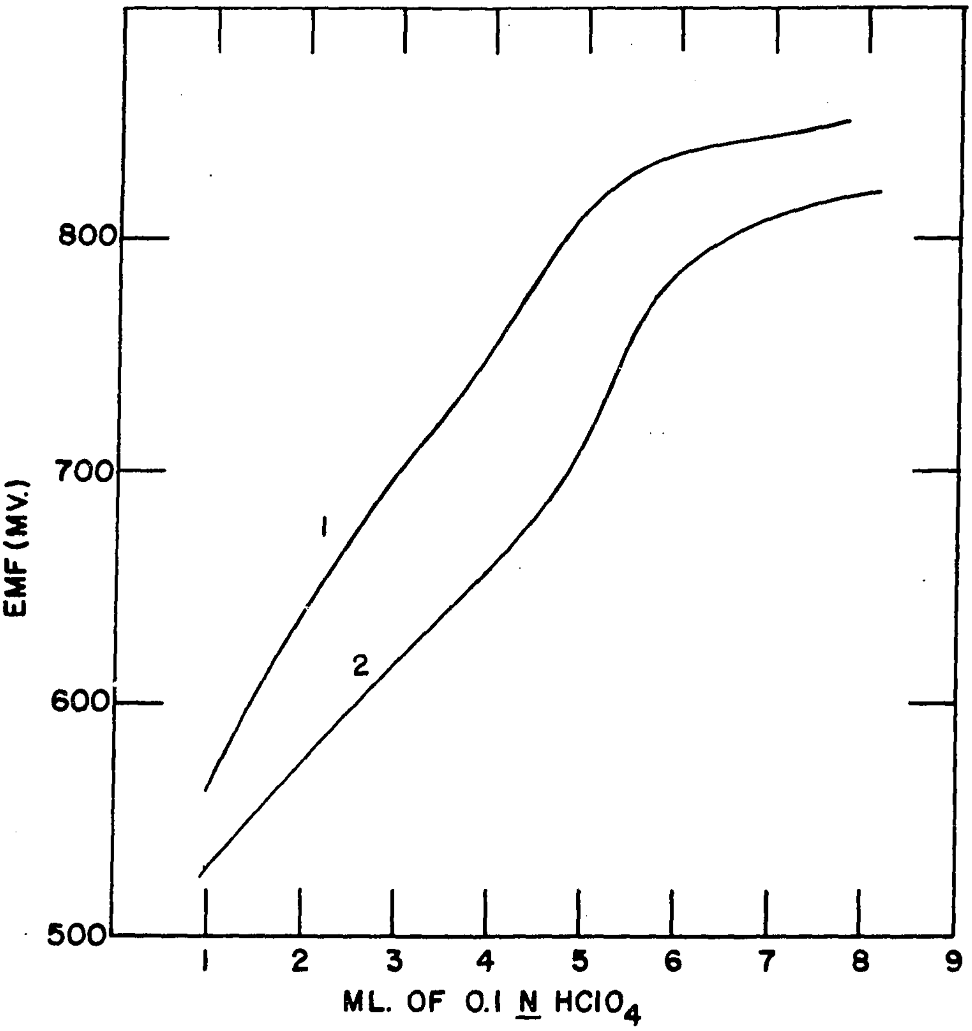


Figure 3. Titration of triphenylphosphine oxide with (1) $HClO_4$ in glacial acetic acid and (2) $HClO_4$ in dioxane

Table 20. Potential break (mv/ml)[a] at the end-point for a given volume of titrant

Compound	5 ml	10 ml	20 ml
tri-*n*-octylphosphine oxide	255	165	--
bis(di-*n*-hexylphosphinyl)methane	--	100	--
bis(dicyclohexylphosphinyl)methane	250	--	--
bis(di-2-ethylbutylphosphinyl)methane	190	--	--
[(di-*n*-octylphosphinyl)-(diphenylphosphinyl)]methane	170	--	--
bis(di-*n*-hexylphosphinyl)ethane	--	65	--
bis(di-*n*-hexylphosphinyl)propane	--	120	65
bis(di-*n*-hexylphosphinyl)butane	--	150	100
acetonyldi-*n*-hexylphosphine oxide	205	--	--
phenacyldi-*n*-hexylphosphine oxide	190	--	--

[a] Defined as the potential 1/2 ml after the end-point minus the potential 1/2 ml before the end-point.

character and lower phosphoryl stretching frequencies. Compounds having phosphoryl groups with the most single bond character will have a greater electron density around the phosphoryl oxygen, and should be the most basic. Burger (3) has shown this to be true, e.g., the degree of extraction of uranium increases as the alkoxy groups in tributyl phosphate are gradually replaced with alkyl groups.

The infrared spectra of the extractants being used in this study were taken using a Beckman IR-7 instrument. The

Table 21. Phosphoryl stretching frequencies

Compound[a]	Frequency in cm^{-1}	
HDPM	1178	1193
EBDPM	1177	1205
EHDPM	1172	1198
TOPO	1170	1185
TEHPO	1168	1202

[a] Dissolved in carbon disulfide.

phosphoryl stretching frequencies are tabulated in Table 21.

The phosphoryl band appears as a doublet with the band at the lower frequency having the greater intensity. The differences in the phosphoryl stretching frequencies are not large enough to allow any relative order of basicities to be established. The small differences that do exist are most likely caused by steric and solvation effects.

Another approach to establishing a relative order of basicity for the extractants is to compare their efficiency in the extraction of an acid. This was done using nitric acid. Ten ml of a 0.05 M solution of the extractant in 1,2-dichlorobenzene was shaken for 10-15 minutes with varying concentrations of nitric acid. The nitric acid in the organic phase was then either titrated directly in the organic phase with tetrabutylammonium hydroxide or stripped with water and titrated with sodium hydroxide. The results are reported in Table 22. Using the extraction of nitric acid as the criterion, then the relative order of basicity is HDPM > EBDPM > EHDPM and TOPO > TEHPO. It should be kept in mind that Siddall (35) has shown that there is only a very rough correlation between the extraction of an acid and the extraction of a metal.

Table 22. Extraction of nitric acid, millimoles acid extracted[a]

cmpd. $[HNO_3]$	HDPM	EBDPM	EHDPM	TOPO	TEHPO
1	0.4710	0.3903	0.3376	0.4530	0.3675
3	0.8885	0.7558	0.5758	0.5115	0.4810
5	0.9860	0.8808	0.7573	0.5295	0.5035
7	1.0295	0.9675	0.8500	0.6130	0.5435
9	1.1110	1.0981	1.0481	0.7445	0.6310

[a] Millimoles acid extracted by 0.5 millimoles compound and corrected for the extraction of acid by the diluent 1,2-dichlorobenzene.

It was mentioned previously that at certain acid concentrations TBP extracts acid in excess of a 1:1 ratio. In the cases under investigation, it was found that when the aqueous nitric acid concentration was high enough the amount of acid extracted exceeded the amount that could be accounted for by a 1:1 reaction with the phosphoryl groups. This makes it seem unlikely that the alkoxy oxygens in TBP are involved with or are the cause of the extraction of the excess nitric acid. The excess acid is probably dissolved nitric acid molecules which may be weakly hydrogen bonded to the initially extracted acid molecules.

Effect of Nitric Acid Concentration on the Distribution Coefficients of Uranium(VI) Nitrate, Thorium Nitrate, and Samarium Nitrate

The distribution of a metal nitrate across the interface between an aqueous and an organic solvent can be described as involving either ion pairs and/or unionized species. Once in the organic phase a reaction with the ligand takes place. Of course in some cases it might be that some of the ligand dissolves in the aqueous phase and forms a complex which then passes into the organic phase. Or possibly the reaction takes place at the interface. In any case, the addition of nitric acid to the aqueous phase will affect the extraction of any metal ion.

Depending on the conditions, nitric acid could either hinder or aid the extraction. The addition of nitric acid would be expected to hinder extraction because of (1) competition of the protons with the metal ions for the available ligand molecules, (2) formation of nonextractable cationic nitrate complexes, and (3) increased solubility of the ligand and/or the complex in the aqueous phase. At the same time adding nitric acid could aid extraction by (1) eliminating hydrolysis of the metal ions, (2) decreasing the dielectric constant of the aqueous phase which would favor the formation of ion pairs, (4) decreasing the activity of the water, (5) the mass action effect of increasing the nitrate ion concentration, and (6) the formation of extractable anionic nitrate complexes.

Acids are extracted by all of the oxonium-type extractants. The complexes formed with acids are much weaker than those formed with metals. However, when the acid concentration is high compared to that of the metal, as it often is, the acid can compete effectively for the extractant molecules. Naito and co-workers (75, 76) have demonstrated this competition effect for the extraction of uranium(VI) nitrate by TBP from a nitric acid solution.

Evidence for complexes between uranium(VI) and nitrate ions has been reported by some while a complete lack of evidence has been reported by others. In the case of equilibrium studies, exact knowledge of the activity coefficients of the ions involved may be causing the discrepencies. Kaplan et al. (263) have shown that the uranium(VI)-trinitrato complex has a quite distinct ultraviolet-visible spectrum which allows it to be identified. The complex can be formed by the addition of tetrabutylammonium nitrate to solutions of uranium(VI) nitrate in acetone, methyl isobutyl ketone, ethyl acetate, or nitromethane. In their opinion the predominant species in 16 M nitric acid solutions is the neutral uranium(VI) dinitrate, with some of the trinitrato complex, $UO_2(NO_3)_3^-$. Jezowska-Trzebiatowska and Chemielowska (264) using conductivity measurements have shown the trinitrato complex to have dissociation constants of 10^{-8} to 10^{-2} depending on the solvent. They have come to the conclusion that uranium(VI) nitrate occurs in organic solvents chiefly in the form of neutral molecules and does not form ion pairs to any great extent. Healy and McKay (44) found no spectral evidence for the extraction of $HUO_2(NO_3)_3$. However, Solovkin (92) has found the formation of $HUO_2(NO_3)_3 \cdot 2TBP$ as a third phase when using high concentrations of nitric acid and TBP. The trinitrato complex probably is not extracted to any extent except under extreme conditions.

Thorium forms somewhat stronger cationic complexes with nitrate than uranium(VI). Thorium has been generally believed not to form anionic complexes, but Danon (265) on the basis of ion exchange studies thinks that anionic complexes are formed in very concentrated (3 M) lithium nitrate solutions. Marple[1] disagrees. The extraction of anionic complexes of

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[1] Marple, L. W., Ames Lab., Ames, Iowa. Anion exchange behavior of uranium and thorium in mixed solvent systems. Private communication. 1963.

thorium with nitrate has not been reported.

In the present study, the extraction of uranium(VI) nitrate, thorium nitrate and samarium nitrate was studied as a function of nitric acid concentration. The results are presented in Table 23. From an examination of the distribution coefficients obtained, it can be seen that a number of generalizations are possible: (1) bis(dialkylphosphinyl)-methanes are better extractants than trialkylphosphine oxides; (2) compounds with straight chain alkyl groups are better extractants than those with branched-chain alkyl groups for both the bis(dialkylphosphinyl)methanes and the trialkyl-phosphine oxides; (3) trialkylphosphine oxides and the more sterically hindered bis(dialkylphosphinyl)methanes are better extractants for uranium(VI) nitrate than for thorium nitrate; and (4) nonsterically hindered bis(dialkylphosphinyl)methanes are better extractants for thorium nitrate than for uranium(VI) nitrate.

The greater solvation possible for the complexes of the diphosphoryl compounds than for the complexes of the mono-phosphoryl compounds undoubtedly accounts for the diphosphoryl compounds being better extractants than the monophosphoryl compounds. That the compounds with straight chain alkyl groups should be better extractants than those with branched-chain alkyl groups is a result of steric effects. HDPM and EBDPM extract thorium better than uranium under the conditions used because the common anion effect is greater

Table 23. Distribution coefficients for the extraction of uranium(VI) nitrate, thorium nitrate, and samarium nitrate

$[HNO_3]$	HDPM[a]	EBDPM[a]	EHDPM[a]	TOPO[a]	TOPO[b]	TEHPO[b]
A. uranium[c]						
1	252	196	132	27.8	388	10.3
3	149	22	96	7.3	84	4.7
5	88	14	74	5.0	42	2.8
7	57	17	55	2.9	24	1.9
B. thorium[c]						
1	409	342	32	2.2	35.0	0.2
3	1009	426	20	0.9	6.0	0.2
5	801	360	14	0.8	4.3	0.2
7	751	341	12	0.9	4.1	0.2
C. samarium[c]						
1	1.23	0.14	0.08		0.14	
3	0.17	0.02	<0.01		0.02	
5	0.03	<0.01	<0.01		<0.01	
7	$\leq$0.01	<0.01	<0.01		<0.01	

[a] Extractant concentration is 0.0500 M.

[b] Extractant concentration is 0.1000 M.

[c] Metal nitrate concentration is 0.01667 M.

for thorium than for uranium. Steric effects have overshadowed the common anion effect for TOPO, TEHPO, and EHDPM. In these cases, uranium is better extracted than thorium.

The extraction of samarium was found to be quite poor and it appears that uranium and/or thorium can be separated from samarium using a variety of reagents and 3-5 M nitric acid. It was found possible to separate uranium from samarium and thorium from samarium using 0.05 M HDPM in 1,2-dichlorobenzene and an aqueous phase 5 M in nitric acid.

The ultra-violet visible spectra of uranium solutions extracted with HDPM were examined for evidence of the uranium(VI) trinitrato complex. No evidence could be found for the existence of this complex in either the organic or aqueous phase, even when the aqueous phase had a nitric acid concentration of 15 M.

In most cases, as the aqueous nitric acid concentration was increased, the distribution coefficients decreased. This, of course, is the result of the competition between the metal nitrate and the nitric acid for the available ligand. In a few cases, the common anion effect exceeds the competition effect and the distribution coefficients increase in going from aqueous phases which are 1 M in nitric acid to those which are 3 M in nitric acid. It is difficult to explain why in three cases the distribution coefficients should increase on going from aqueous phases which are 5 M to 7 M in nitric acid reversing the trend set for aqueous phases of lower acid concentrations. This was found for the extraction of thorium by 0.05 M TOPO and 0.10 M TEHPO and for the extraction of uranium(VI) by 0.05 M EBDPM. Horner and Coleman (225) have reported similar behavior for the extraction of plutonium(IV) nitrate by TOPO and by TEHPO as has Weaver (266) for the extraction of neptunium(IV) nitrate by TOPO. Other reported cases include the extraction of plutonium(VI) nitrate (223), thorium perchlorate (208), and uranium(VI) perchlorate (267) by TOPO. The simplest explanation would be that anionic species are being extracted at high acid concentrations. However, this does not seem very likely in view of the fact that perchlorates have not been shown to form anionic species with metal ions.

Existence of Rotational Isomers for Sterically Hindered Extractants

A high density of electrons on the phosphoryl oxygen will be of little value in coordinating a metal atom if the electrons are not sterically available. It was of interest to see if any of the extractants being used showed evidence of having rotational isomers.

The infrared spectra of a wide variety of organophosphorous compounds show the phosphoryl band as what appears to be a doublet. Numerous explanations have been offered to account for this. Phosphoryl dipole-dipole interaction has been suggested for trimethylphosphine oxide (268). In triphenylphosphine oxide it may be the interaction of the aromatic rings with phosphoryl groups of adjacent molecules (229). Sterically hindered compounds like tris(2-ethylhexyl)-phosphine oxide undoubtedly have different configurations (229). Popov et al. (269) believe that the existence of different configurations is the explanation for trimethyl phosphate rather than dipole-dipole interaction as proposed for trimethylphosphine oxide or coupling between the phosphoryl and methoxy vibrations as proposed by Gore (270).

The first type of experiment performed was the examination of the infrared film spectra of HDPM, EBDPM, EHDPM, and TEHPO at room temperature and at liquid nitrogen temperature. The stretching frequencies for the phosphoryl bands are given in Table 24.

Table 24. Phosphoryl stretching frequencies (cm^{-1}) at room and liquid nitrogen temperatures[a]

Cmpd. \ temp.	25°C		-210°C	
HDPM	1163	?	1163	1192
EBDPM	1168	1204	1160	1204
EHDPM	1166	1195	1161	1197
TEHPO	1164	1199	1159	1197

[a] Film spectra.

In all cases, the absorption band in the doublet with the lower frequency was of greater maximum intensity than the absorption band with the higher frequency. This intensity differential was greater at -210°C than it was at 25°C as is shown in Table 25.

Table 25. Relative absorbances[a] for the bands in the phosphoryl doublet

temp. / Compd.	25°C	-210°C
HDPM	--	1.45
EBDPM	1.43	3.18
EHDPM	1.18	2.28
TEHPO	1.24	1.92

[a] Computed by dividing the absorbance of the low frequency band by that of the high frequency band.

It was hoped that by lowering the temperature sufficiently one band of the phosphoryl doublet would disappear. Usually only a single isomer is stable in the solid state if a crystalline lattice is formed. In the present situation, the solid states may be more of an amorphous glassy nature in which case the spectra will be similar to the liquid state. At any rate, the change in the intensity ratio for the bands in the doublet upon cooling is taken as an indication of a change in the equilibrium between isomeric forms. Fermi resonance which has been proposed by Shuler (110) to account for the phosphoryl doublet of TBP is not temperature dependent. Phosphoryl dipole-dipole interactions cannot be ruled out as a cause of the doublet. However, it seems unlikely that such interactions are strong enough to cause a splitting of the phosphoryl band. For instance molecular weight determinations of HDPM, EBDPM, and TOPO in benzene have shown them to be monomers[1].

Proton magnetic resonance spectra were also obtained for the various extractants and examined for evidence of rotational isomers. A Varian Associates model HR-60 high resolution nuclear magnetic resonance spectrometer was used. Samples were dissolved in either carbon tetrachloride or deutero chloroform. Tetramethylsilane was used as an internal standard.

It was felt that if isomers existed, then not all of the methyl groups would be equivalent in a given molecule. Therefore, more spin-spin splittings would be observed than the usual triplet. However, in the cases investigated only a triplet was found. This does not indicate that rotational isomers do not exist. It does indicate that if they do exist their life-time is not long enough to be observed.

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[1] O'Laughlin, J. W., Ames Lab., Ames, Iowa. Molecular weight determinations. Private communication. 1963.

Table 26. Chemical shift of methyl groups in NMR spectra

Compound	Shift[a]	Splittings
HDPM	0.90 ppm	3
EBDPM	0.90 ppm	3
TOPO	0.88 ppm	3
TEHPO	0.90 ppm	3

[a] Downfield shift from tetramethylsilane, measured from peak of maximum intensity in the triplet.

Saturation of Extractants with Thorium Nitrate

A frequently used method of obtaining information about the ligand:metal ratio in a complex is to saturate a solution of the ligand with the metal. It is assumed, of course, that the complex is stable enough so that at "saturation" the concentration of the free ligand will be quite small. In the case of complexes with TBP, this method apparently works with metal nitrates such as uranium(VI) nitrate, thorium nitrate, and cerium(III) nitrate but not for cobalt(II) nitrate or aluminum nitrate (44).

Ten ml of a dilute solution (usually 0.001 M) of the extractant was equilibrated with solid thorium nitrate pentahydrate for 25 hours or longer or with a 1 M solution of thorium nitrate for 10 to 15 minutes. The organic phase was then analyzed for thorium using the nonaqueous thorin method. The results are reported in Table 27.

The lowest ligand:metal ratios obtained were 1.88 for TOPO, 2.03 for TEHPO, 1.15 for HDPM, and 1.24 for EBDPM. The degree of saturation varied with the nature of the diluent used. The more polar solvent gave the greater degree of saturation. The solvents themselves were not found to dissolve or extract amounts of thorium nitrate which could be detected either by means of infrared spectra or by analysis with thorin.

Using these data as a guide, the existence of the $Th(NO_3)_4 \cdot 2TOPO$, $Th(NO_3)_4 \cdot 2TEHPO$, $Th(NO)_3)_4 \cdot HDPM$, and $Th(NO_3)_4 \cdot EBDPM$ are postulated. In addition, $Th(NO_3)_4 \cdot TOPO$ may exist to a slight extent to account for the ligand:metal ratio dropping below two for saturation in 1,2-dichloroethane. Ross and White (208) have reported that when a solution of TOPO in cyclohexane is saturated with an aqueous solution of thorium nitrate a ligand:metal ratio of 3:1 results in the organic phase. However, their aqueous phase was 1 M in nitric acid and considerable amounts of nitric acid were extracted along with the thorium nitrate according to their own determinations. The coextraction of nitric acid should have been taken into account in calculating the ligand:metal ratio; it was not. Zingaro and White (205) obtained the same results as Ross and White. In this case the acid concentration of the aqueous phase was low enough so that very little coextraction of nitric acid along with the thorium nitrate occurred. The most

Table 27. Saturation of extractants with thorium nitrate

Method of saturation	Ligand	Solvent	Ligand:metal ratio in organic phase at saturation
a	HDPM	1,2-dichloroethane	1.15
a	HDPM	"	1.16
a	HDPM	1,2-dichlorobenzene	1.43
a	HDPM	"	1.45
a	HDPM	"	1.48
a	HDPM	"	1.46
b	HDPM	1,2-dichlorobenzene	1.58
b	HDPM	"	1.57
b	HDPM	"	1.57
a	EBDPM	1,2-dichloroethane	1.25
a	EBDPM	"	1.24
a	EBDPM	1,2-dichlorobenzene	1.37
a	TOPO	1,2-dichlorobenzene	2.04
a	TOPO	cyclohexane	2.01
a	TOPO	"	2.02
a	TOPO	"	2.04
b	TOPO	1,2-dichloroethane	1.88
b	TOPO	"	1.92

---

[a] Crystalline thorium nitrate pentahydrate.

[b] 1 *M* aqueous thorium nitrate.

Table 27. (Continued)

Method of saturation	Ligand	Solvent	Ligand:metal ratio in organic phase at saturation
b	TOPO	1,2-dichlorobenzene	2.07
b	TOPO	"	2.10
b	TOPO	"	2.10
b	TOPO	cyclohexane	2.30
b	TOPO	"	2.33
b	TOPO	"	2.31
c	TOPO	cyclohexane	2.78
c	TOPO	"	2.75
a	TEHPO	1,2-dichlorobenzene	2.03
a	TEHPO	"	2.07
a	TEHPO	cyclohexane	2.27
a	TEHPO	"	2.27

---

[c] 10 ml of 0.05 M TOPO equilibrated with 10 ml of 0.5 M thorium nitrate.

favorable conditions for saturation that they used were an organic phase with an initial concentration of 0.05 M TOPO in cyclohexane aqueous phase with an initial concentration of thorium nitrate of 0.50 M. These conditions simply are not sufficient for saturation of the TOPO. Repeating their work, it was found that under these conditions a ligand:metal ratio of 2.8:1 was obtained while using other conditions lower ligand:metal ratios could be obtained.

The solvent dependence of the degree of saturation indicates that equilibria exist between the postulated species and other species with the former being better solvated by the more polar solvents. Under saturation conditions, when the ligand molecules are in short supply, the diluent is capable of competing with the ligand for solvation of the thorium nitrate. As will be shown later, the nitrates in the just postulated complexes are covalent as indicated from their infrared spectra.

Infrared Studies on the Nature of the Extractable Species with Thorium Nitrate and Various Ligands

Phosphoryl bonding

The ligands under study bond to metal ions through the oxygen of the phosphoryl group. It is, therefore, of interest to examine the infrared characteristics of the bonded and nonbonded phosphoryl group.

Several workers (270, 271, 272) have calculated the stretching frequency for the phosphoryl group using the equation for a simple harmonic oscillator. The force constant must be known and this can be estimated by using Gordy's rule (273).

A. Gordy's rule

$$k = 1.67N\left(\frac{X_A X_B}{d^2}\right)^{3/4} + 0.30$$

k = force constant x 10^{-5} dynes/cm

N = bond order

X_A, X_B = electronegativities of atoms A and B

d = internuclear distance in angstroms

B. Simple harmonic oscillator

$$\nu_{\text{cm}^{-1}} = 1307 \frac{\sqrt{k}}{\sqrt{\mu}}$$

$$\frac{1}{\mu} = \frac{1}{m_a} + \frac{1}{m_b}$$

ν = frequency in cm^{-1}

k = force constant x 10^{-5} dynes/cm

μ = reduced mass

m_a, m_b = masses of atoms a and b in amu

For the purpose of calculations the bond order is taken to be two although the semipolar nature of the bond is well established (274-277). Some results are shown in Table 28. Absorption frequencies calculated in this manner give results of the right order of magnitude but are not very accurate. In practice, the stretching frequency for the non-bonded phosphoryl group varies from 1160-1400 cm^{-1} (269).

A second way to calculate the frequency of the phosphoryl band for a given molecule is to use empirical correlation

Table 28. Calculated phosphoryl stretching frequencies

Experimental frequency	Calc. freq.	$P\rightarrow O$ bond dist. in angstroms	Cmpd.	Ref.
--	1190 cm^{-1}	1.46	$(RbPO_3)_n$	271
1280 cm^{-1}	1221 cm^{-1}	1.39	P_4O_{10}	270
1290 cm^{-1}	1112 cm^{-1}	1.58	$POCl_3$	270

which have been developed between the phosphoryl frequency and the nature of the substituents. Daasch and Smith (278) noticed that there was a correspondence between the frequency of the phosphoryl band and the electronegativity of the substituent groups. Bell *et al*. (239) give an equation of the form:

$$\lambda \text{ (microns)} = \frac{39.96 - \Sigma X}{3.995}$$

The term "X" is called the "phosphoryl absorption shift constant" and is directly related to the electronegativities of the substituent groups. Griffin (279) uses a similar equation:

$$\nu \text{ (cm}^{-1}) = 16.80 \, \Sigma \, \sigma^* + 1198$$

In this case Taft substituent constants (σ^*) are used as a measure of electronegativity. Another relationship is that given by Zingaro and Hedges (229):

$$\nu \text{ (cm}^{-1}) = 1172 + 13.86 \, \Sigma \, \sigma^* + 4.11 \, \Sigma \, E_s$$

Here, the stretching frequency is related to both Taft's polar substituent constant (σ^*) and to his steric substituent constant (E_s). Very good correlations can be obtained using these empirical methods providing all the spectra used in obtaining the correlation are run in the same manner. Complications arise when the phosphoryl band occurs as a doublet.

Force constants have been calculated using "linear coordinate analysis" type methods (280-282). It is interesting to note that such calculations have shown that the frequency of the phosphoryl vibration for molecules of the type POX_3 is quite insensitive to changes in the mass of atom X, the length of the P-X bond, and the bond angles (280).

Table 29. Force constants for the phosphoryl bond

Molecule	$k \times 10^{-5}$ $dyne \cdot cm^{-1}$	Ref.
F_3PO	11.4	281
Cl_3PO	10.0	281
Br_3PO	9.6	281
Me_3PO	8.2	282

In Table 30 is given the reported phosphoryl stretching frequencies for a number of trialkylphosphine oxides. As discussed by Cotton et al. (283), the main effect observed when a metal is complexed with phosphoryl groups is a decrease

Table 30. Phosphoryl stretching frequencies for trialkylphosphine oxides

Phosphine oxide	Solvent or state	P-O freq. (cm^{-1})	Ref.
trimethyl	mull	1170	278
trimethyl	KBr	1174	283
trimethyl	--	1176	282
tri-n-propyl	--	1166	284
tri-n-butyl	mull	1157	3
tri-n-butyl	CS_2	1169	229
tricyclohexyl	CS_2	1143	229
tri-n-octyl	CS_2	1161	229
tri-n-octyl	CS_2	1170	285
tri-n-octyl	CCl_4	1169	229
tri-n-octyl	CCl_4	1154	286
tri-n-octyl	cyclohexane	?	286
tri-n-octyl	liquid	1165	286
tri-n-octyl	solid	1144	229
tri-n-octyl	solid	1142	285
tri-n-octyl	solid	1143	286
tris(2-ethylhexyl)	CS_2	1198, 1164	229
tris(2-ethylhexyl)	CS_2	1160	286
tris(2-ethylhexyl)	CCl_4	1155	286
tris(2-ethylhexyl)	solid	1150	286

in the amount of $p\pi$ - $d\pi$ back bonding in the $^{-}O \rightarrow P^{+}$ group which decreases the bond order and lowers the absorption frequency. The extent to which the phosphoryl stretching frequency is lowered is called the "phosphoryl frequency shift". The decrease in bond order is confirmed by X-ray studies showing an increase in P-O bond length upon complexation.

Nadig (47) found a rough linear correlation between the ionic potential (charge of cation/ionic radius of cation) of a solute in an organic phase containing TBP and the phosphoryl frequency shift. A similar relationship was found for solutes in TOPO. The phosphoryl frequency shift is taken as a measure of the strength of the complex formed. Solutes with the highest ionic potentials would be expected to form the strongest bonds with the extractant. Also, the maximum distribution coefficient of a metal nitrate between an organic phase containing TBP and an aqueous phase, was found to increase as the ionic potential of the cation increased. His work with the rare earths revealed an interesting phenomenon. The phosphoryl stretching frequency shifts indicate that the strength of the TBP-rare earth nitrate complexes increase with decreasing atomic number from lutetium to lanthanum, with the exception of erbium. However, in the absence of nitric acid, the distribution coefficients of the rare earth nitrates increase with increasing atomic number from lanthanum to gadolinium and then decrease (174). This illustrates the fact

Table 31. P-O bond lengths

Compound	P-O bond length, Å	Ref.
$(CH_3)_3PO$	1.48	287
$SbCl_5\cdot(CH_3)_3PO$	1.61	288
$Co[(CH_3)_3PO]_2(NO_3)_2$	1.54	289
$UO_2(NO_3)_2\cdot 2(EtO)_3PO$	1.52	290, 291

that the strengths of the complexes in both phases must be considered before any relative order of extraction can be predicted for certain. In general, though, the greater the phosphoryl frequency shift the higher the distribution coefficient will be according to Oshima (77).

Studies on crystalline complexes lead one to believe that if the extractant forms more than one complex with a given metal, then the phosphoryl frequency shift increases as the ligand:metal ratio decreases. Thus, the phosphoryl frequency shift is greater for $SbCl_3\cdot(CH_3)_3PO$ than for $SbCl_3\cdot 2(CH_3)_3PO$ (292), greater for $HgCl_2\cdot(C_6H_5)_3PO$ than for $HgCl_2\cdot 2(C_6H_5)_3PO$ (293), and greater for $5HgCl_2\cdot 2(CH_3)_3PO$ than for $HgCl_2\cdot(CH_3)_3PO$ (293). But the shifts for $TiCl_4\cdot 2POCl_3$ and $(TiCl_4\cdot POCl_3)_2$ are identical (294).

In some cases the phosphoryl band is split into several bands upon coordination. The theory of Walmsley and Tyree (295) is that there will be splitting if the metal is coordinated by two or more monodentate ligands (or one or more bidentate ligands) and some other kind of atom or atoms. There will be no splitting if the ligand completely fills the first coordination sphere of the metal or if only one monodentate ligand plus some other kinds of atoms are in the coordination sphere of the metal.

Nitrate bonding

Gatehouse *et al*. (296) and Bertin *et al*. (297) have devised criteria by which it is possible to distinguish between the nitrate ion and the nitrato group in metal nitrates. There is a decrease in symmetry in going from the nitrate ion (point group D_{3h}) to the nitrato group (point group C_{2v}). This causes the NO_2 asymmetric stretching frequency (1380 cm^{-1} in KNO_3) to split into two bands occurring in the regions 1530-1480 cm^{-1} and 1290-1250 cm^{-1}. In addition, the $-O-NO_2$ stretching frequency, theoretically inactive for nitrate ion, occurs as a strong band in nitrato complexes within the range 1034-970 cm^{-1}.

Miller and Wilkins (298) studied a number of ionic nitrates and found bands in the regions 840-815 cm^{-1} (ν_2) (medium) and 1380-1350 cm^{-1} (ν_3) (very strong) in all cases. The presence of other bands occurred with less regularity. It seems, therefore, that the presence of a strong band in the region 1380-1350 cm^{-1} indicates ionic nitrate while strong bands in the regions 1531-1481 cm^{-1}, 1290-1253 cm^{-1}, and

1034-970 cm^{-1} indicate covalent nitrate.

One other thing must be kept in mind in order to identify covalent nitrate. The splitting of the NO_2 stretching frequency must be of the order of 100 cm^{-1} or more. This restriction is necessary to allow for the possible splitting in ionic nitrates caused by an asymmetry of the external electrical field. Katzin (299) found a splitting of 65 cm^{-1} for the ionic nitrates in the lithium nitrate-tri-n-butyl phosphate complex. The smallest splitting he observed for a compound definitely containing nitrato groups was 125 cm^{-1} for the calcium nitrate-tri-n-butyl phosphate complex. However, it may be that a quite large splitting can be obtained with ionic nitrates under certain circumstances. The infrared spectrum of $Th(NO_3)_4 \cdot 4H_2O$ is typical of that attributed to a covalent nitrate compound with $(\nu_4-\nu_1)$ splitting of the order of 200 cm^{-1}. On gradual dehydration ionic nitrate bands begin to appear. Cho and Wadsworth (300) postulate that strong hydrogen bonding between lattice nitrate and lattice water causes the nitrate ion to assume C_{2v} symmetry as in the case of a covalent nitrate. Loss of water, therefore, destroys the hydrogen bonding and allows the nitrate ion bands to appear.

A nitrato group can be bonded in any one of several ways. In fact, Addison (301) gives four ways in which the nitrate can be covalently bonded.

Table 32. Nitrate bands according to Gatehouse *et al*. (296)

			(theoretically inactive) N-O str.	NO$_2$ def.	planar rock	
	NO$_2$ asym. str.					
ionic nitrate	1390 cm^{-1}		1050 cm^{-1}	831 cm^{-1}	720 cm^{-1}	
	ν_3		ν_1	ν_2	ν_4	
	ν_4	ν_1	ν_2	ν_6	ν_5	ν_3
covalent nitrate	1531-1481 cm^{-1} NO$_2$ asym. str.	1290-1253 cm^{-1} NO$_2$ sym. str.	1034-970 cm^{-1} N-O str.	800-781 cm^{-1} nonplanar rock	planar rock; asym. bend	NO$_2$ sym. bend

Table 33. Nitrato bonding types

Compound	Type	Evidence	Ref.
$Be_4O(NO)_3)_6$	4	X-ray	301
$Cu(NO_3)_2$	3	IR, X-ray	302
$Cu(NO_3)^+NO_3^-$	4	X-ray	303
$UO_2(NO_3)_2 \cdot 6H_2O$	2	X-ray	304
$UO_2(NO_3)_2 \cdot 2TEP^a$	2	X-ray	290, 291
$UO_2(NO_3)_2 \cdot 6H_2O$	ionic	X-ray	305
$UO_2(NO_3)_2 \cdot 2H_2O$	2	X-ray	306
$UO_2(NO_3)_3^-$	2	X-ray	307
$NbO(NO_3)_3$	4	IR	308
$Co(NO_3)_2[(CH_3)_3PO]_2$	2	X-ray	289
$Ni(NO_3)_3^=$	2	spectral, magnetic	309
$Cu(NO_3)_4^=$	2	spectral, magnetic	309
$Co(NO_3)_4^=$	2	spectral, magnetic	309

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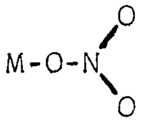
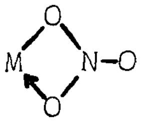
[a] TEP represents triethyl phosphate.



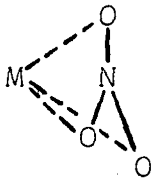
(1)

monodentate



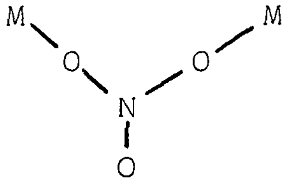
(2)

bidentate



(3)

tridentate



(4)

bridging

Experimental

Infrared spectra were obtained with a Beckman IR-7 infrared spectrophotometer. Irtran-II cell windows were used so that there would be no possibility of anion exchange between the solutions and the cell windows. The cells used were matched with approximately a 0.10 mm inside cell width. A solvent blank was used in the reference beam. 1,2-Dichloroethane was used as the solvent for solutions of HDPM and EBDPM. Carbon tetrachloride was used for solutions of TOPO and TEHPO. All the solutions were prepared by dissolving varying amounts of thorium nitrate pentahydrate in solutions of the extractants. The final concentration of the extractant in all cases was 0.800 mm/10 ml or 0.0800 $\underline{M}$.

HDPM The infrared spectra indicate that HDPM forms at least two complexes with thorium nitrate. The most intense complex band occurs at ~ 1118 cm^{-1}. A plot of the absorbance of this band versus the amount of thorium nitrate shows a break in the slope at a ligand:metal ratio of 2:1 but a continuing increase in intensity indicates still another complex. Saturation data would lead one to expect the second complex to be a 1:1 complex. Another complex band occurs at 1150 cm^{-1}. The slope of the plot of the absorbance of this band versus the amount of thorium nitrate has a break at a ligand:metal ratio of 1.45:1. However, because this weak band is in the neighborhood of several strongly absorbing bands it would be somewhat risky to assign this band to a 3:2 complex.

Covalent nitrate bands are at 1500-1525 cm^{-1}, 1029 cm^{-1}, and ~ 1300 cm^{-1}. The shape of the broad band absorbing at 1300 cm^{-1} indicates that it may be a triplet. In addition, at high ligand:metal ratios there is a broad ionic nitrate band at ~ 1350 cm^{-1}. The plot for this band shows a break in slope at a ligand:metal ratio of 2.96:1. The plots for the covalent nitrate bands show no breaks in the slopes except for the one of the N-O stretching band at 1029 cm^{-1} which changes slope at a 2:1 ratio. Apparently, differences in covalent character in nitrate bonding show up in the N-O stretching band before they do in the NO_2 stretching bands. This would be expected since the N-O stretch involves the oxygen to which the metal atom is bonded. A list of the important infrared bands is given in Table 34. The plots of the absorbances of the bands versus thorium nitrate content are shown in Figures 5-11.

The plot for the absorbance of the free phosphoryl band as a function of the amount of thorium nitrate shows that there is considerable absorption remaining at this frequency even as saturation is approached. This could be interpreted as indicating that at least some of the ligand molecules are monodentate. A second interpretation would be that there is an underlying absorption band.

Table 34. Infrared bands of $Th(NO_3)_4 \cdot xHDPM$ complexes

Band (cm^{-1})	Assignment
1170-1177	free phosphoryl
1118	complex
1150	complex
1500-1525	v_4 covalent nitrate
~1300	v_2 covalent nitrate
1029	v_1 covalent nitrate
~1350	v_3 ionic nitrate

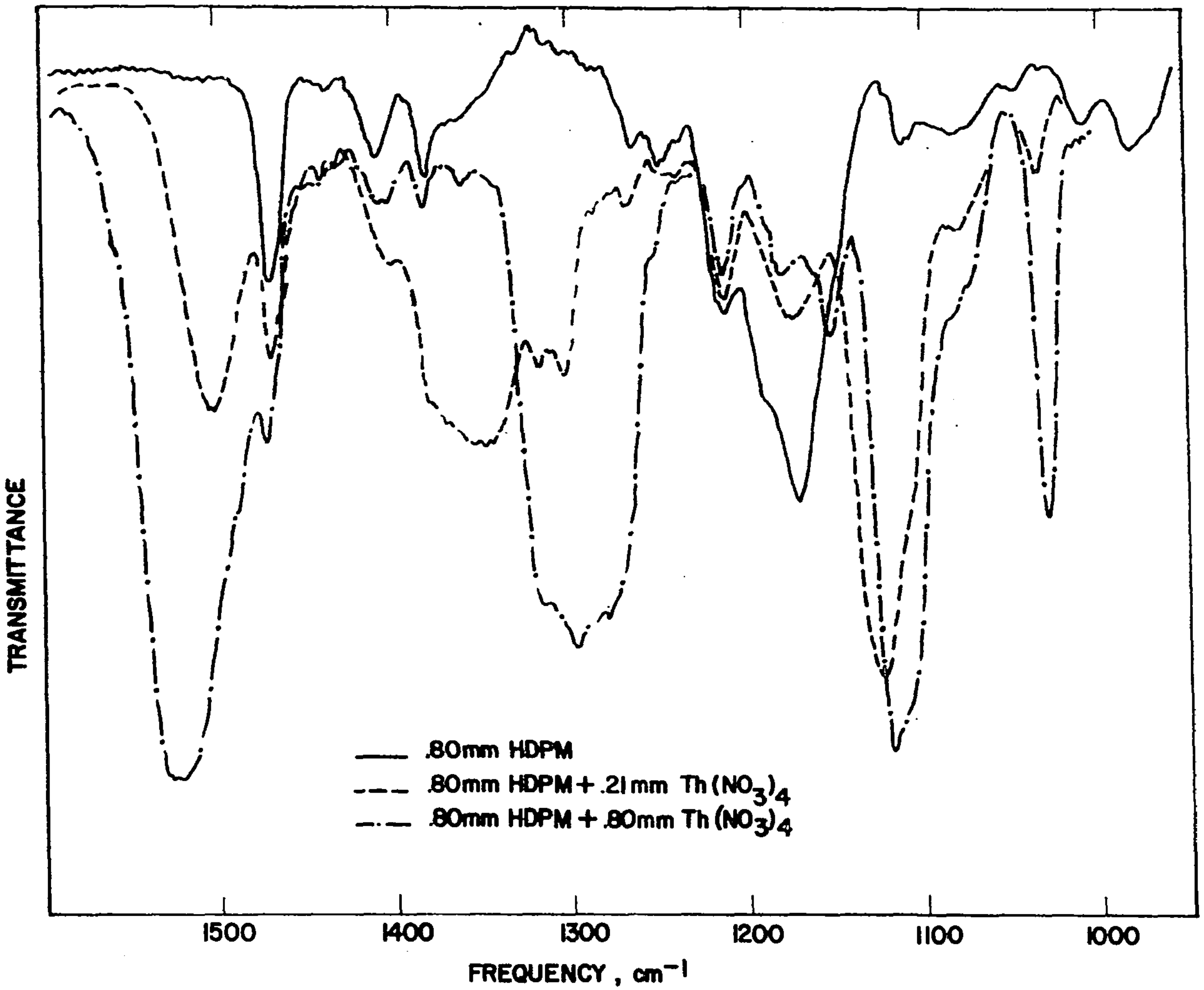


Figure 4. Infrared spectra of the HDPM-Th$(NO_3)_4$ system

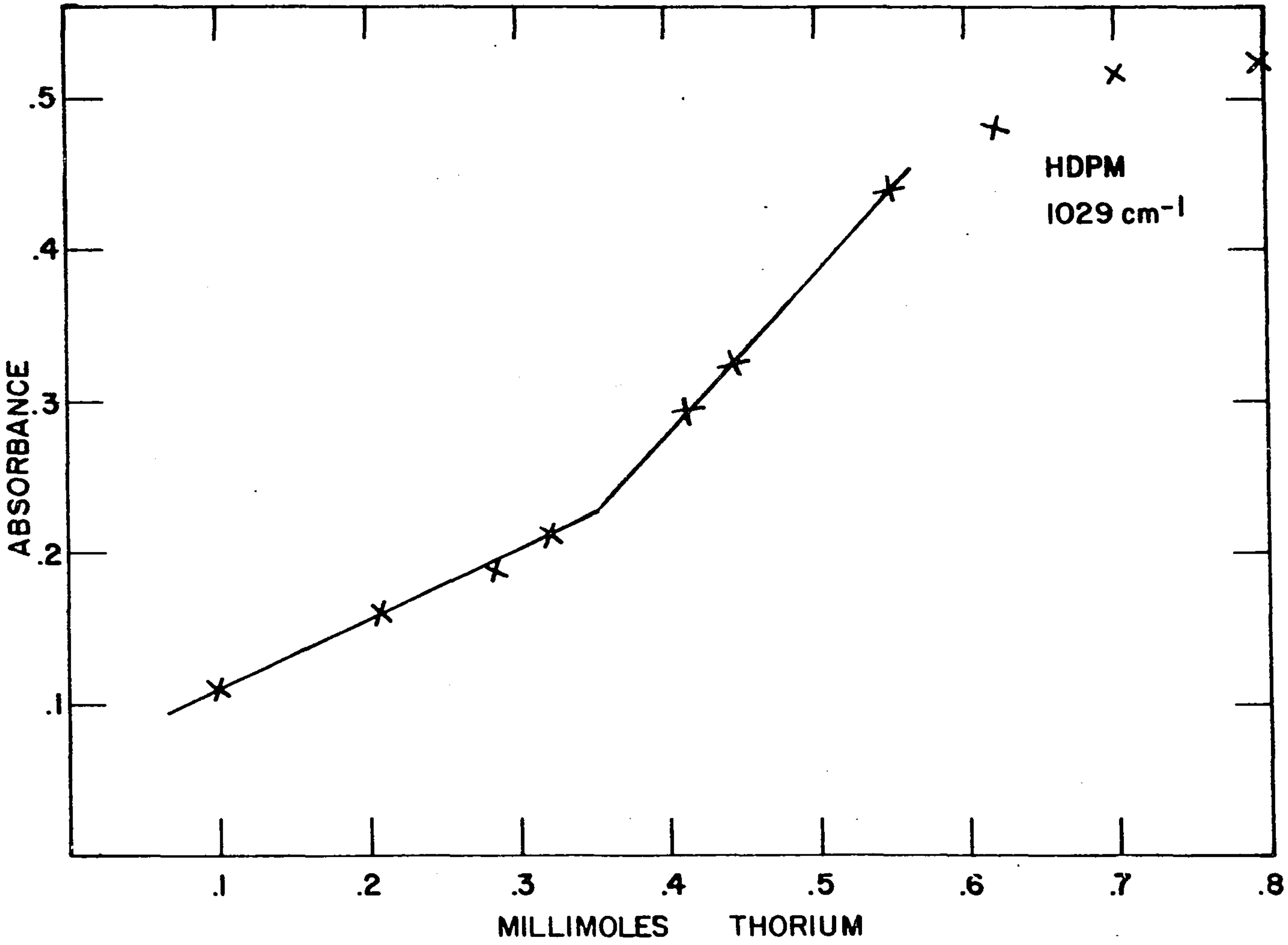


Figure 5. Absorbance of the ν_1 covalent nitrate band as a function of thorium nitrate content

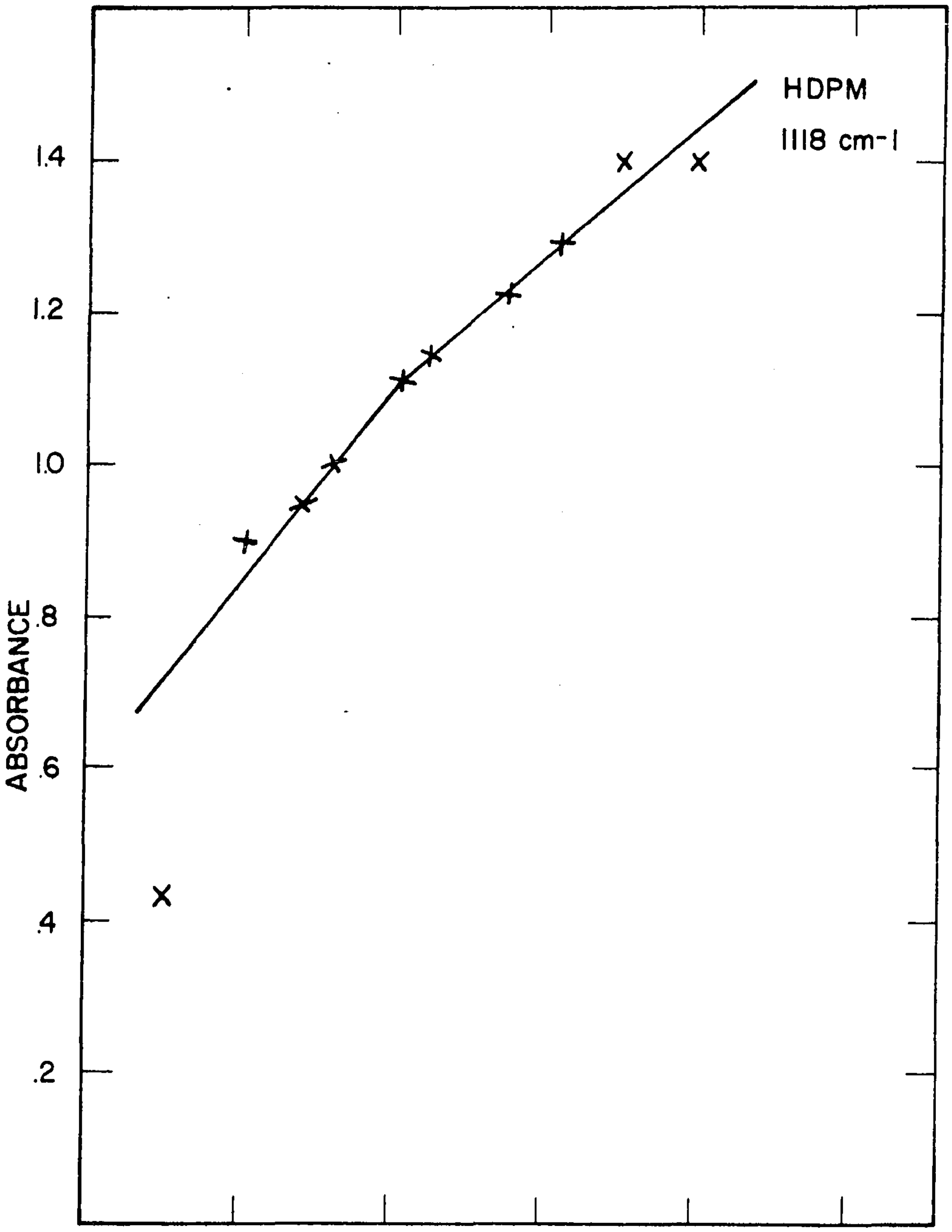


Figure 6. Absorbance of a complex band as a function of thorium nitrate content

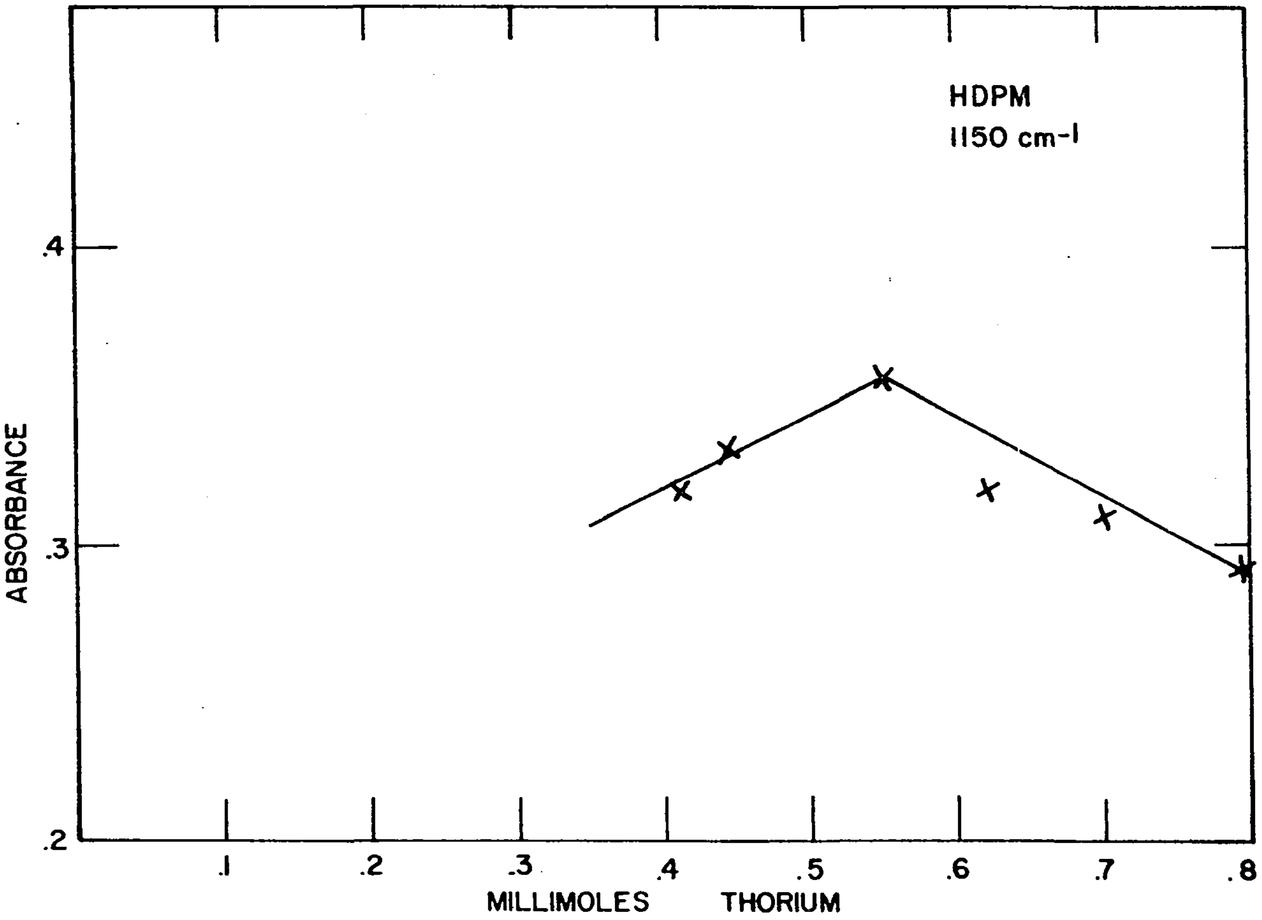


Figure 7. Absorbance of a complex band as a function of thorium nitrate content

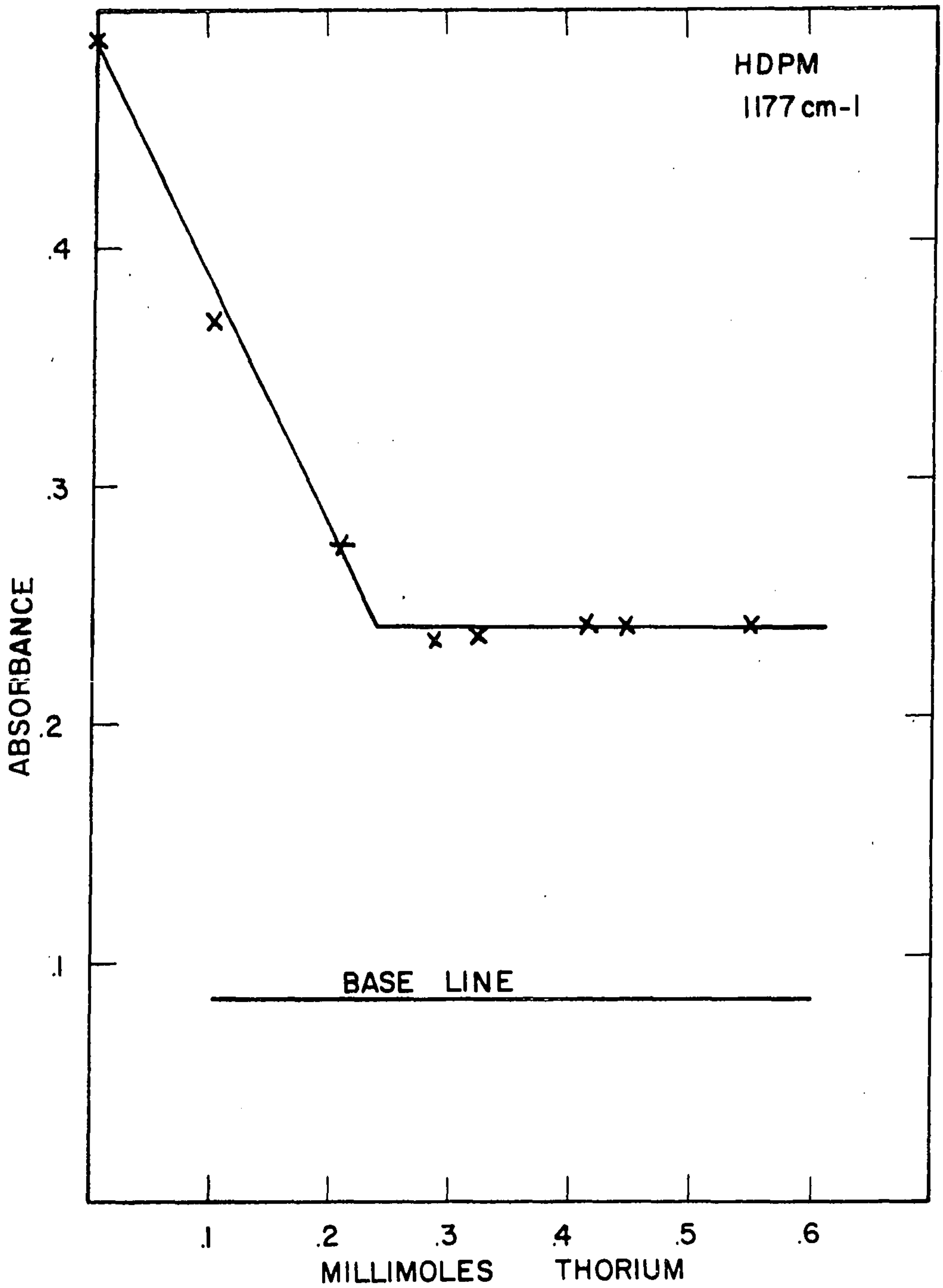


Figure 8. Absorbance of the free phosphoryl band as a function of thorium nitrate content

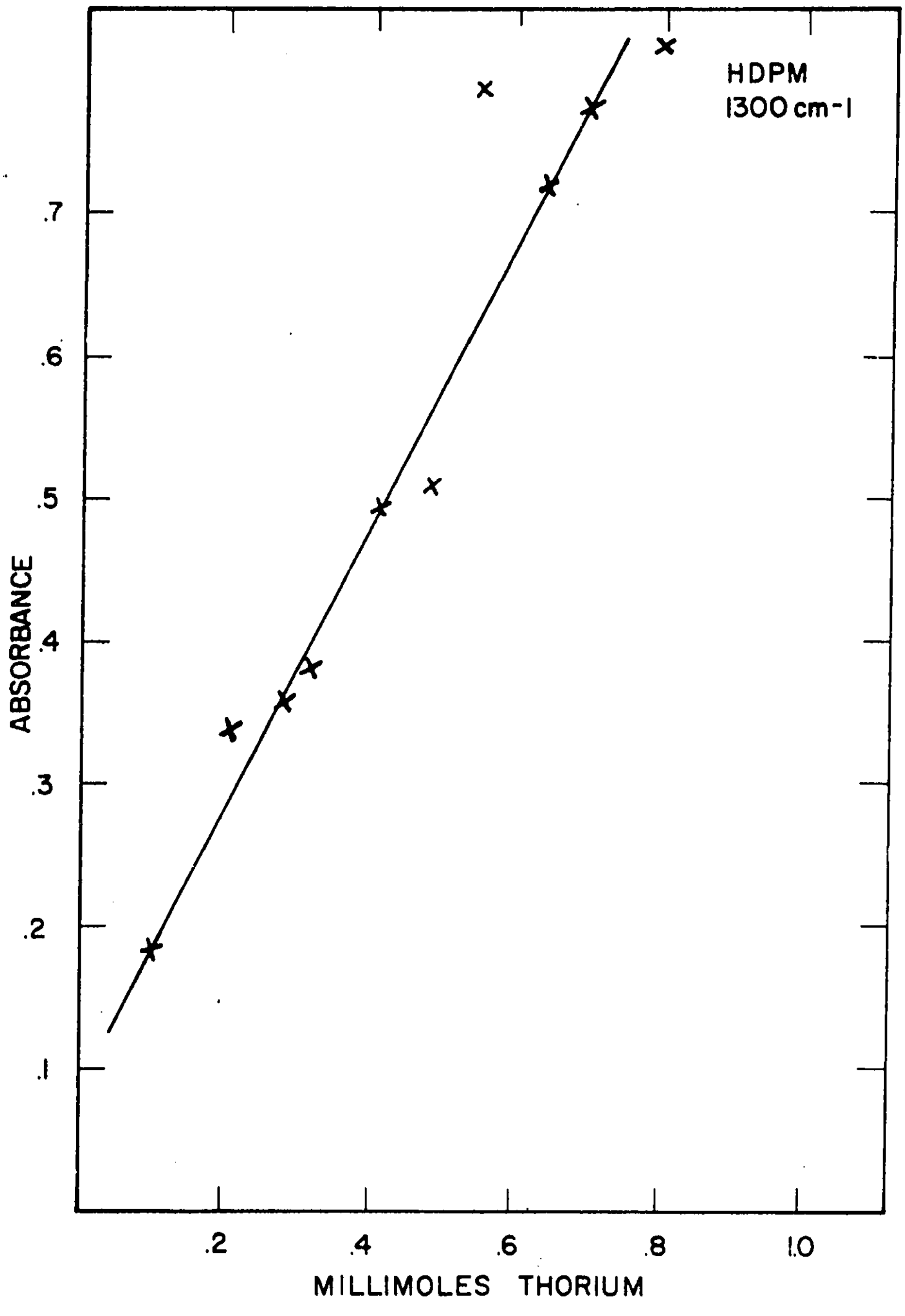


Figure 9. Absorbance of the ν_2 covalent nitrate band as a function of thorium nitrate content

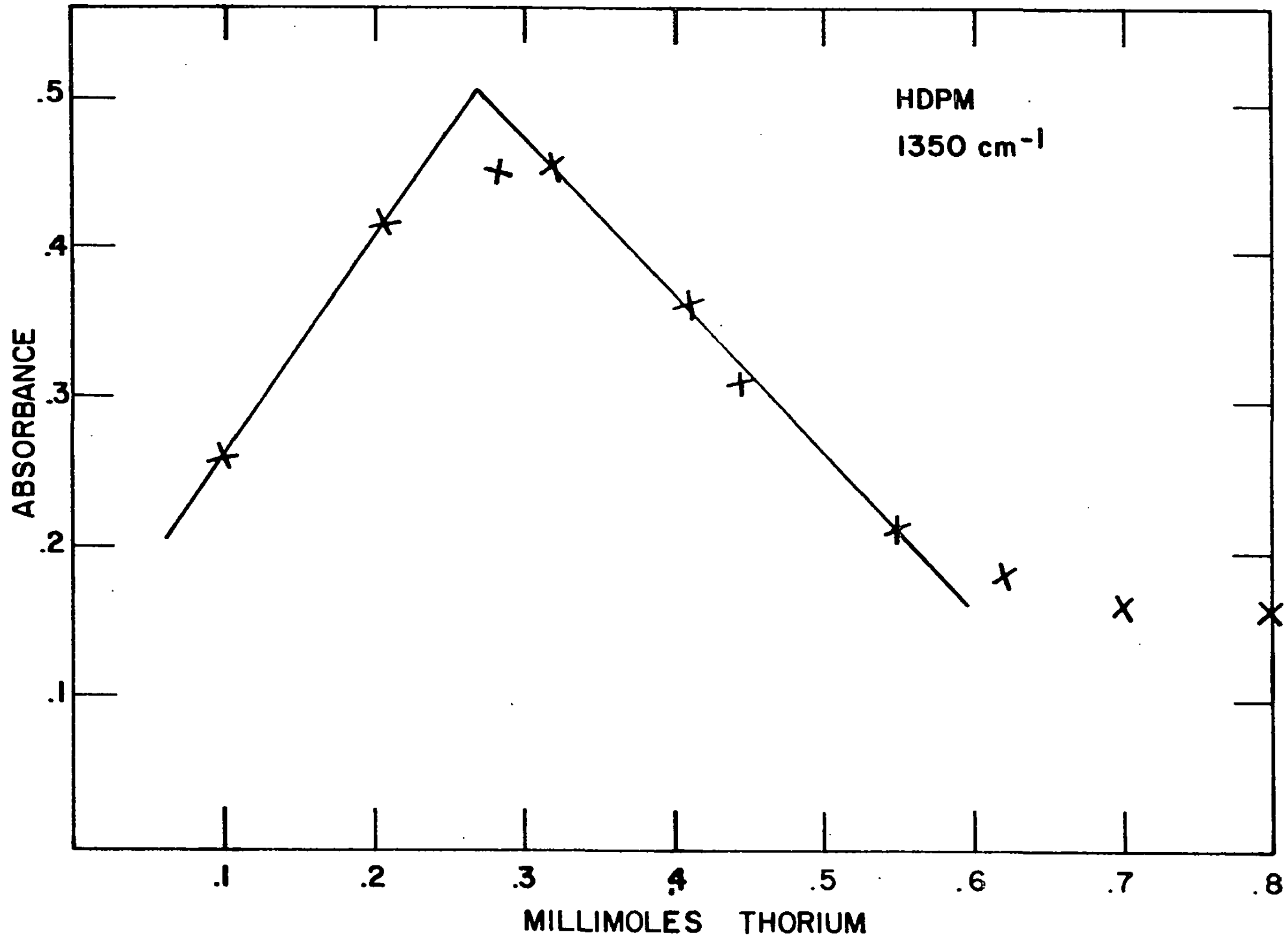


Figure 10. Absorbance of the ν_3 ionic nitrate band as a function of thorium nitrate content

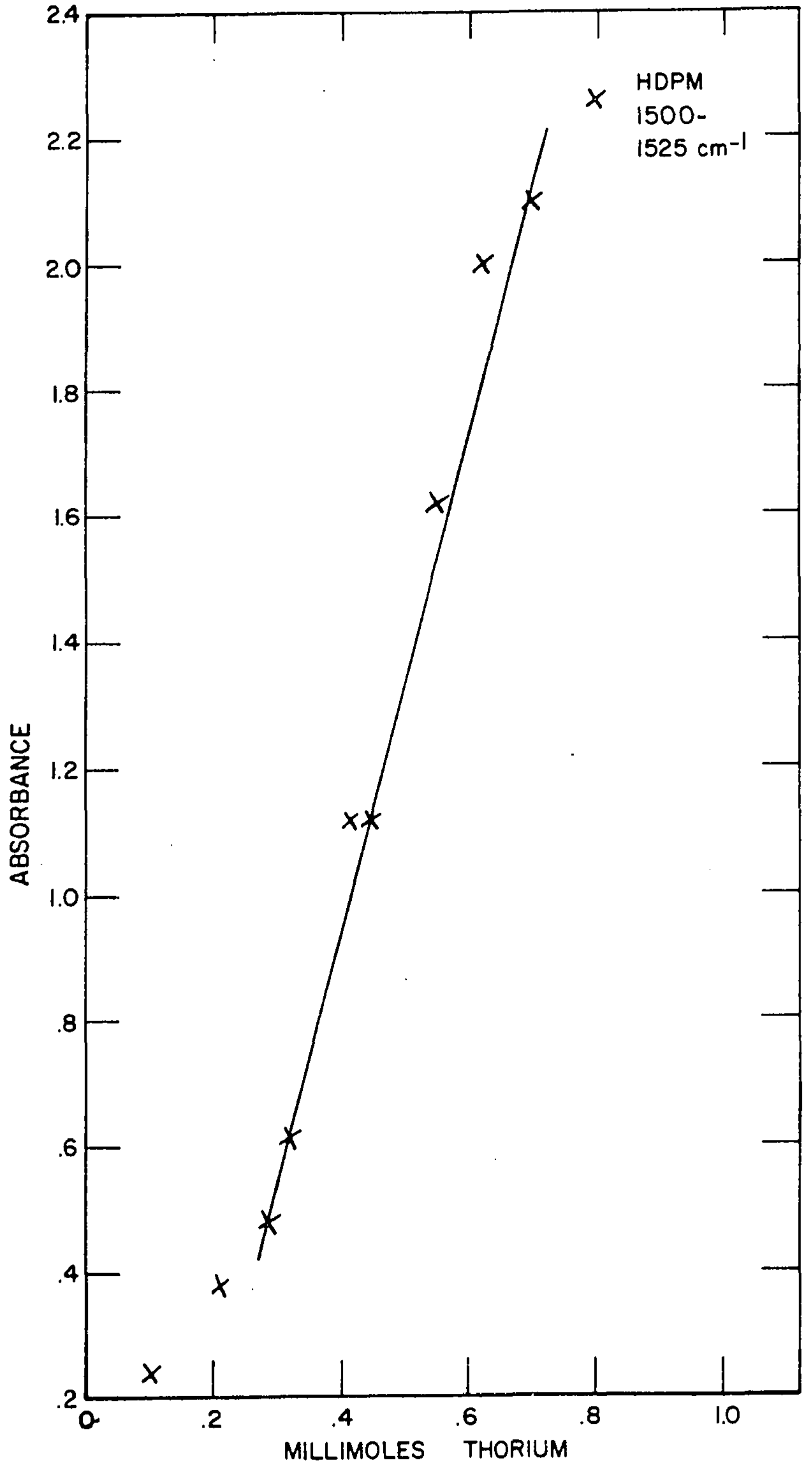


Figure 11. Absorbance of the ν_4 covalent nitrate band as a function of thorium nitrate content

EBDPM An intensely absorbing complex band is found at 1100 cm^{-1}. A plot of the absorbance of this band versus the amount of thorium nitrate shows a slight maximum at a 2:1 ligand metal ratio and then a leveling off in intensity. This is interpreted as evidence for the existence of a 2:1 complex and another complex with an absorption band in much the same place. In view of the saturation data, the other complex may be a 1:1 complex. A complex band also occurs at 1150 cm^{-1} which is attributed to the 2:1 complex. The band at 1075 cm^{-1} may be a complex band and/or a ligand band.

Strong covalent nitrate bands are found at 1522 cm^{-1}, 1026 cm^{-1}, and there is a broad band at ~ 1279 cm^{-1} which is probably a composite of at least two nitrate bands. In addition, at high ligand-metal ratios there is a broad band at ~ 1357 cm^{-1} which can be attributed to the presence of ionic nitrate. This could be associated with the formation of a 3:1 complex or just ionization of the 2:1 complex. The plot shows a break in slope for this band at a ligand:metal ratio of 2.7:1. Table 35 gives a list of the important infrared bands. Figures 13-20 show the plots of the absorbances of the bands versus thorium nitrate content.

As in the case of the HDPM-$Th(NO_3)_4$ system, the plot for the free phosphoryl band shows that there is considerable absorption remaining at the frequency of absorption for the free phosphoryl band even as saturation is approached.

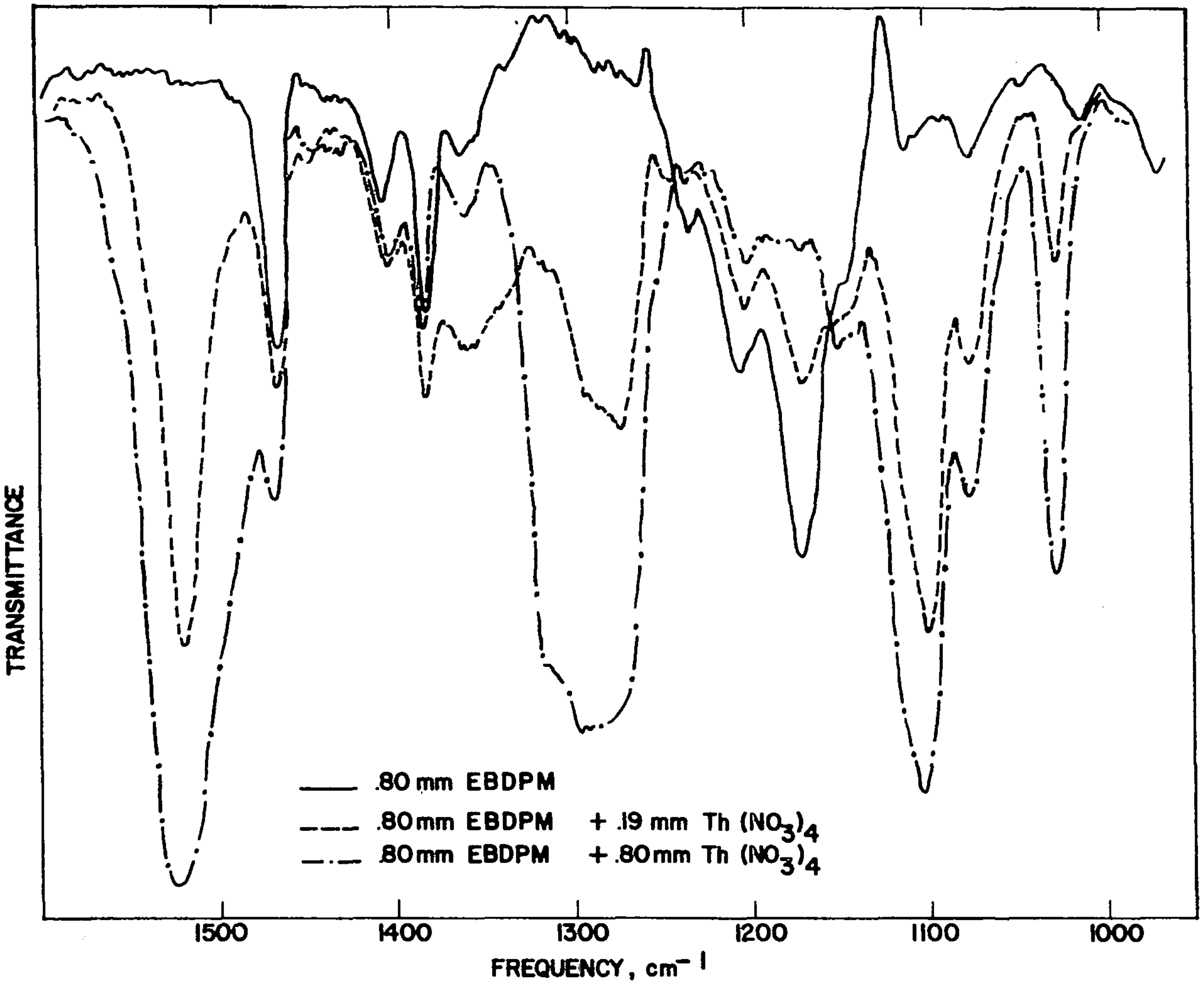


Figure 12. Infrared spectra of the EBDPM-Th$(NO_3)_4$ system

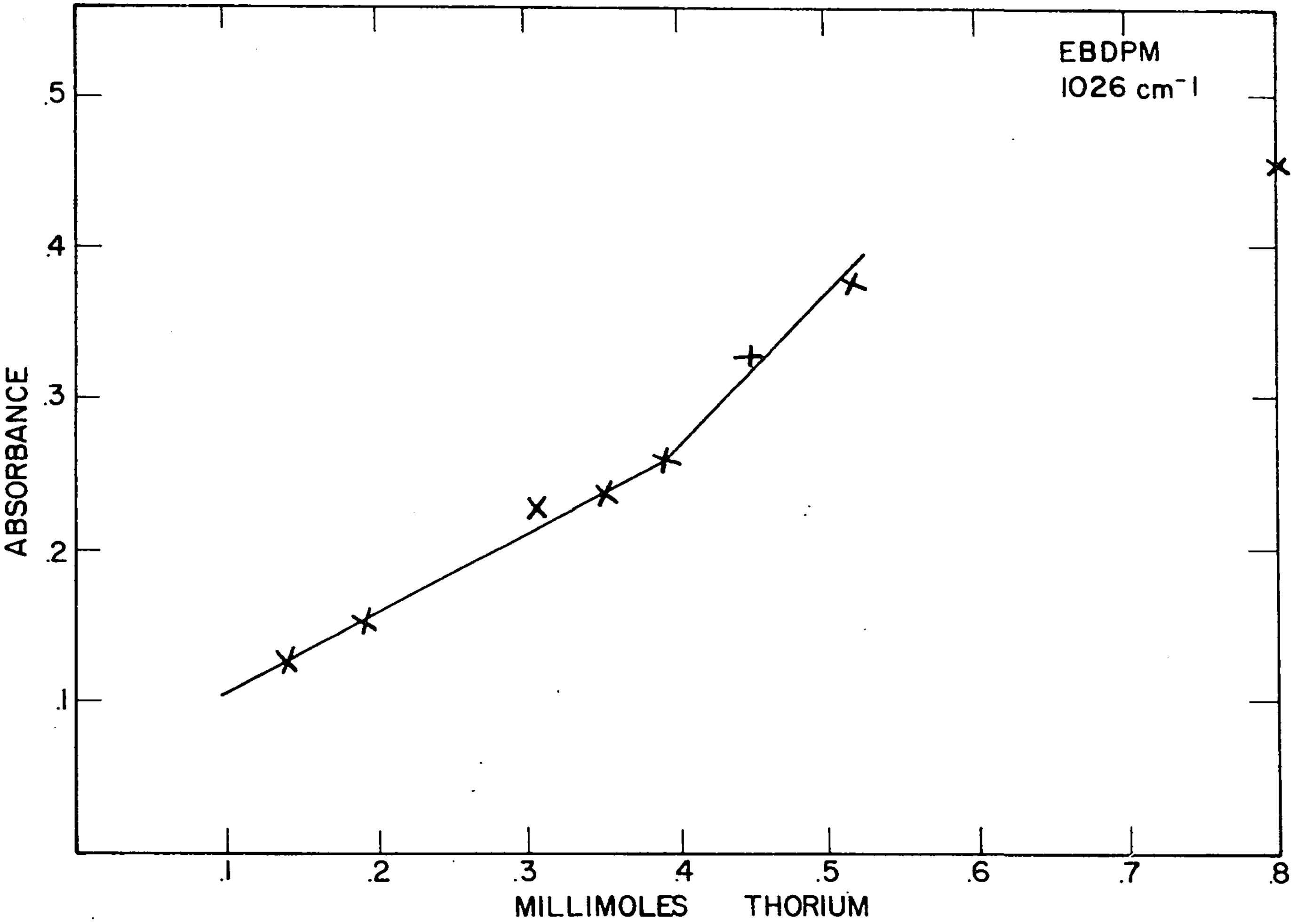


Figure 13. Absorbance of the ν_2 covalent nitrate band as a function of thorium nitrate content

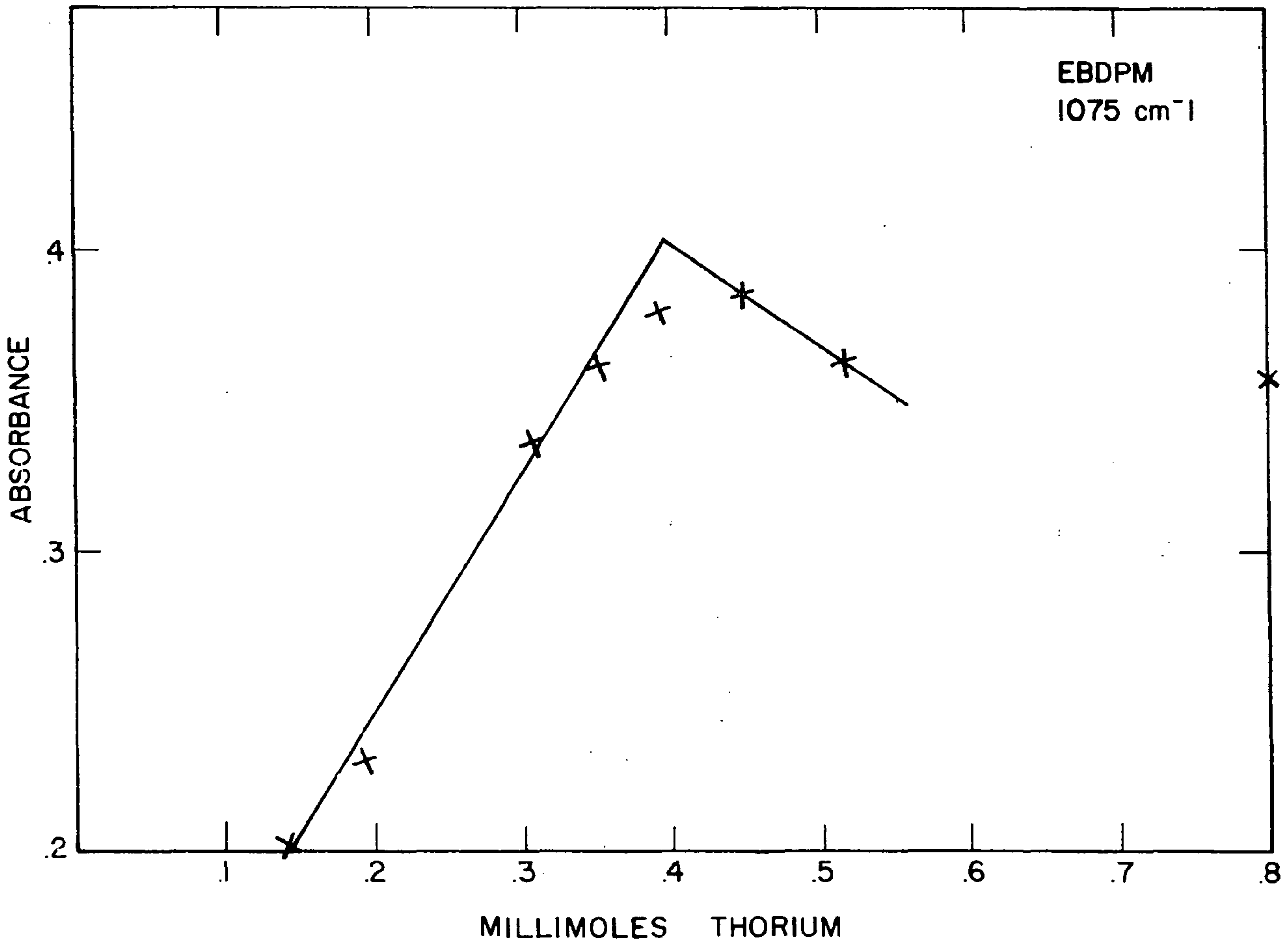


Figure 14. Absorbance of a complex band as a function of thorium nitrate content

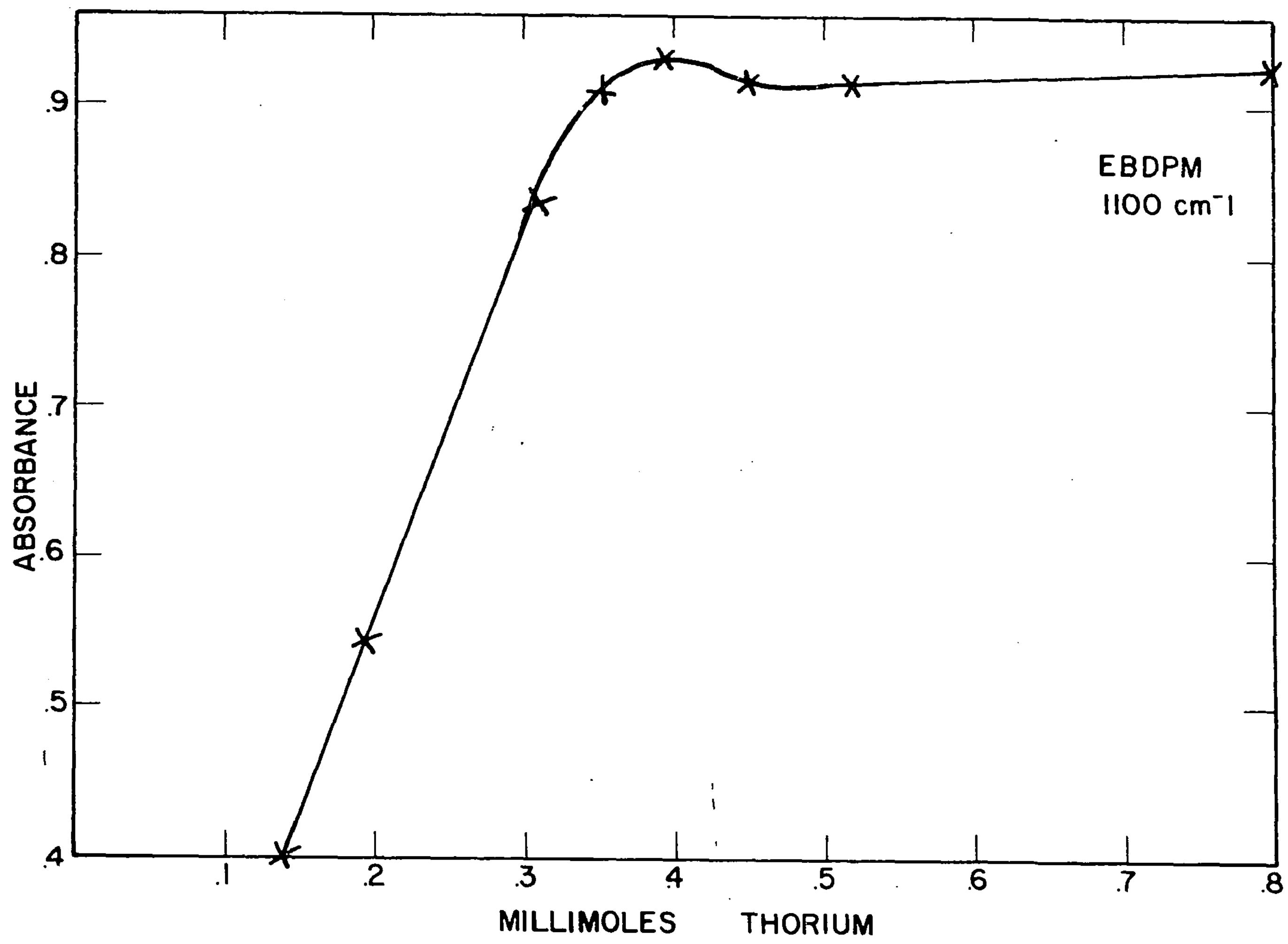


Figure 15. Absorbance of a complex band as a function of thorium nitrate content

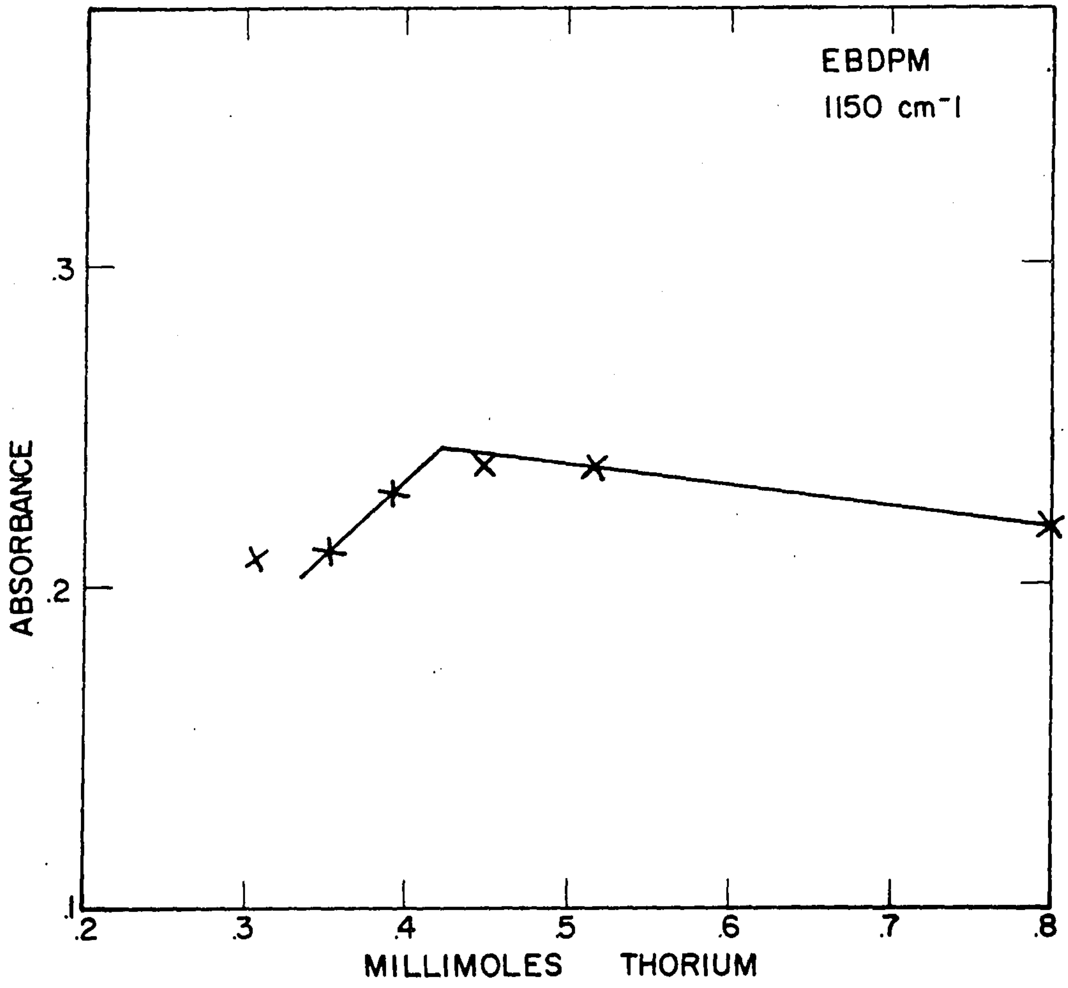


Figure 16. Absorbance of a complex band as a function of thorium nitrate content

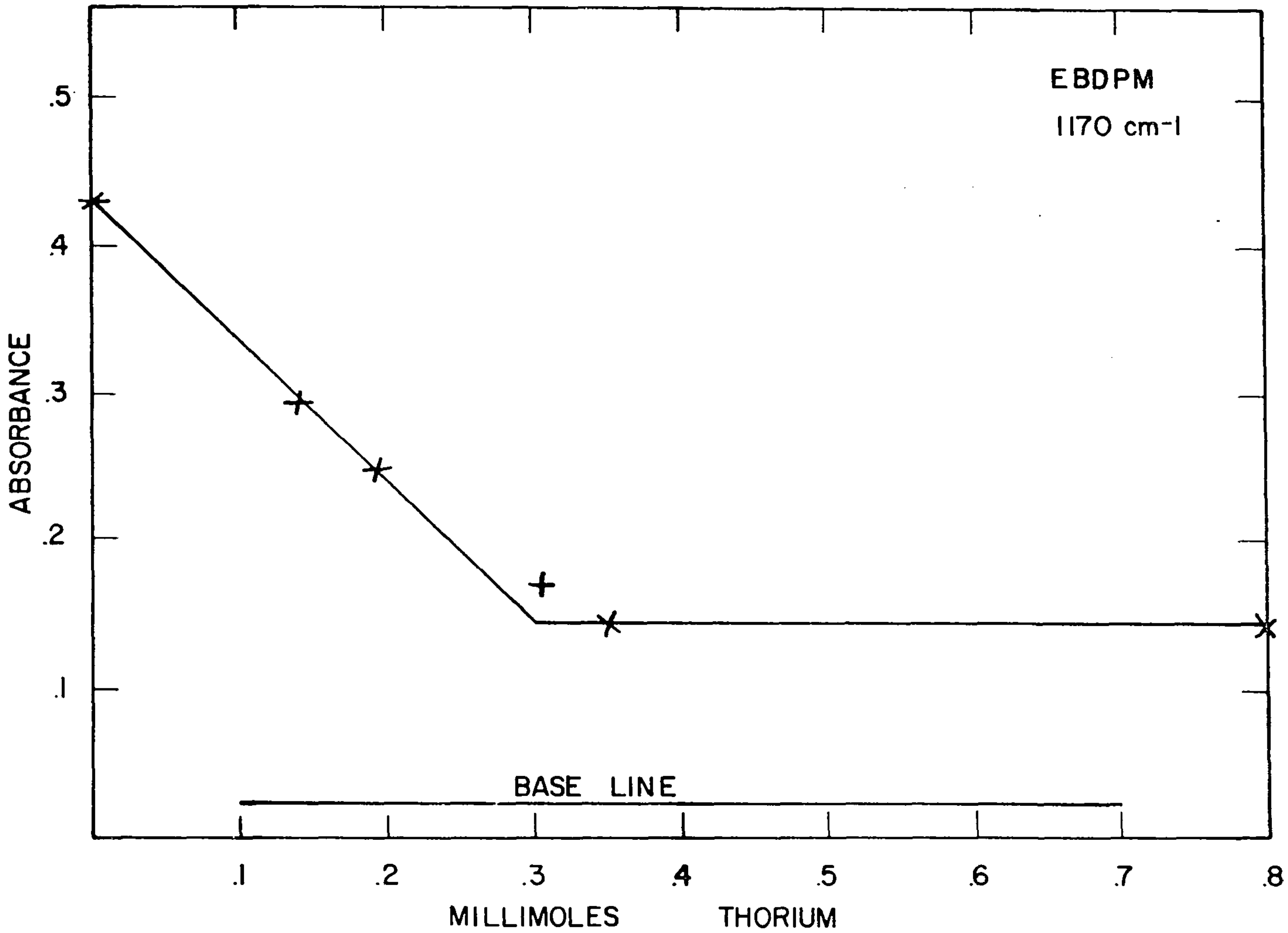


Figure 17. Absorbance of the free phosphoryl band as a function of thorium nitrate content

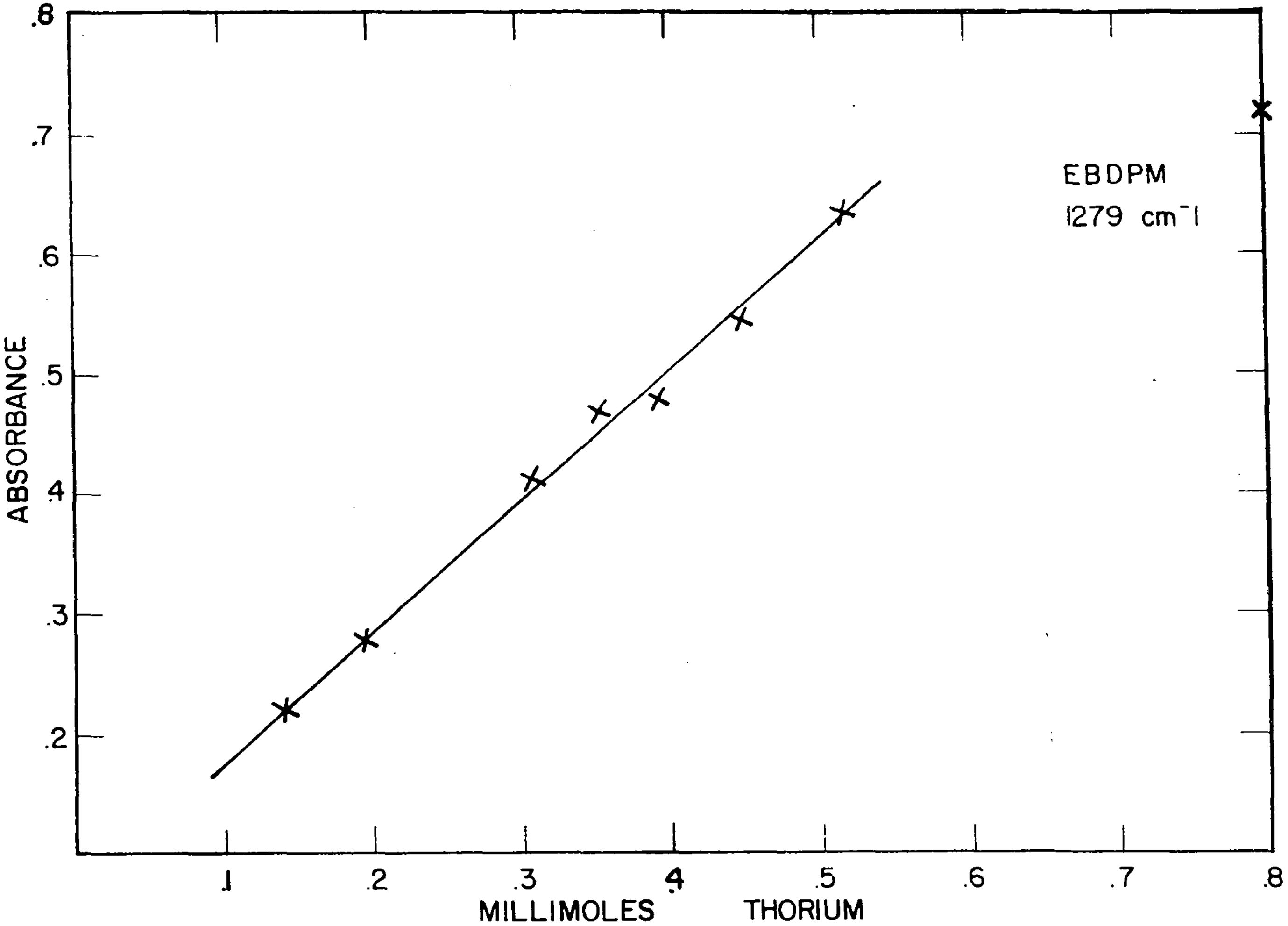
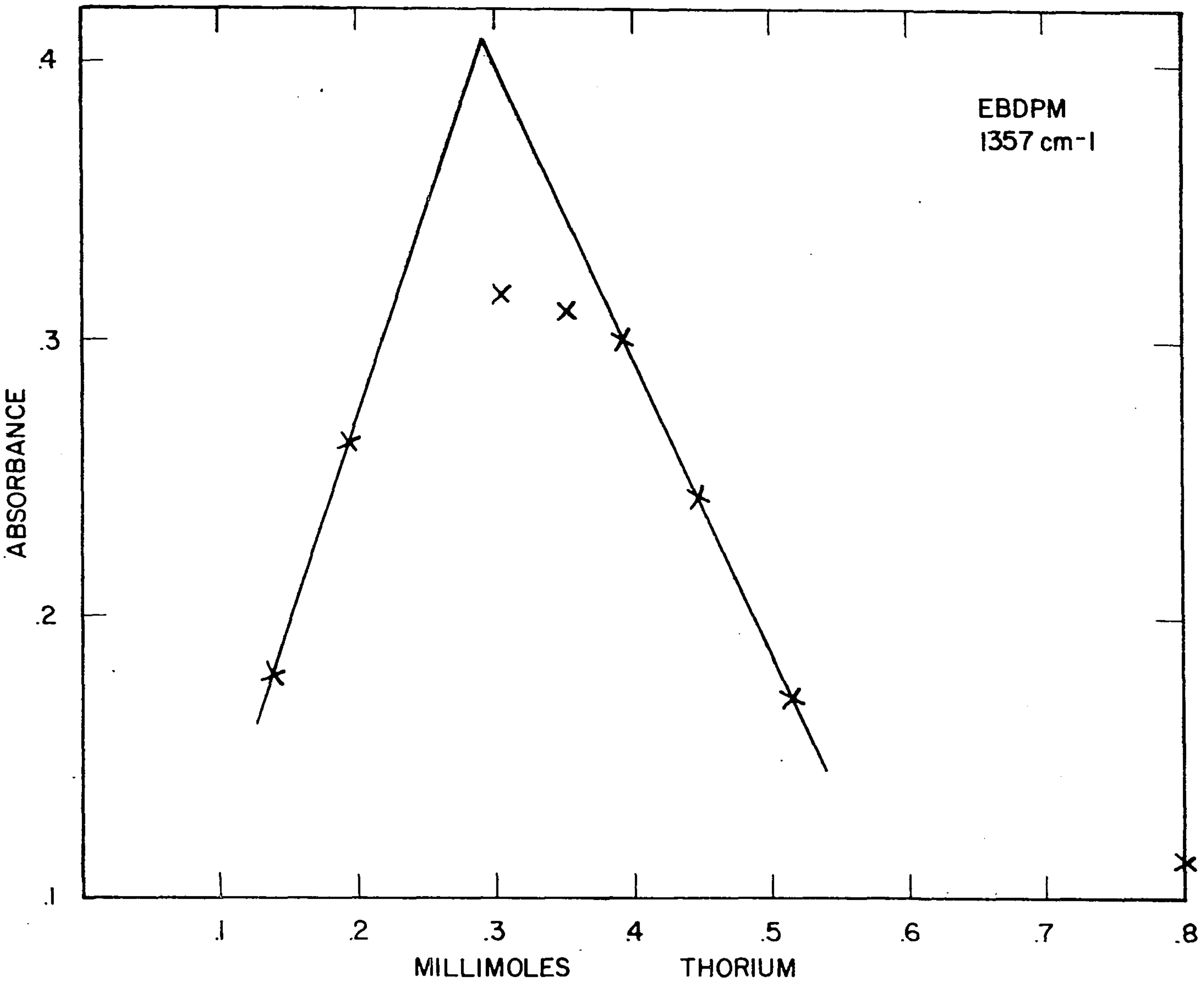


Figure 18. Absorbance of the ν_1 covalent nitrate band as a function of thorium nitrate content

Figure 19. Absorbance of a v_3 ionic nitrate band as a function of thorium nitrate content


EBDPM
1357 cm-1
ABSORBANCE
.4
.3
.2
.1
.1
.2
.3
.4
.5
.6
.7
.8
MILLIMOLES THORIUM

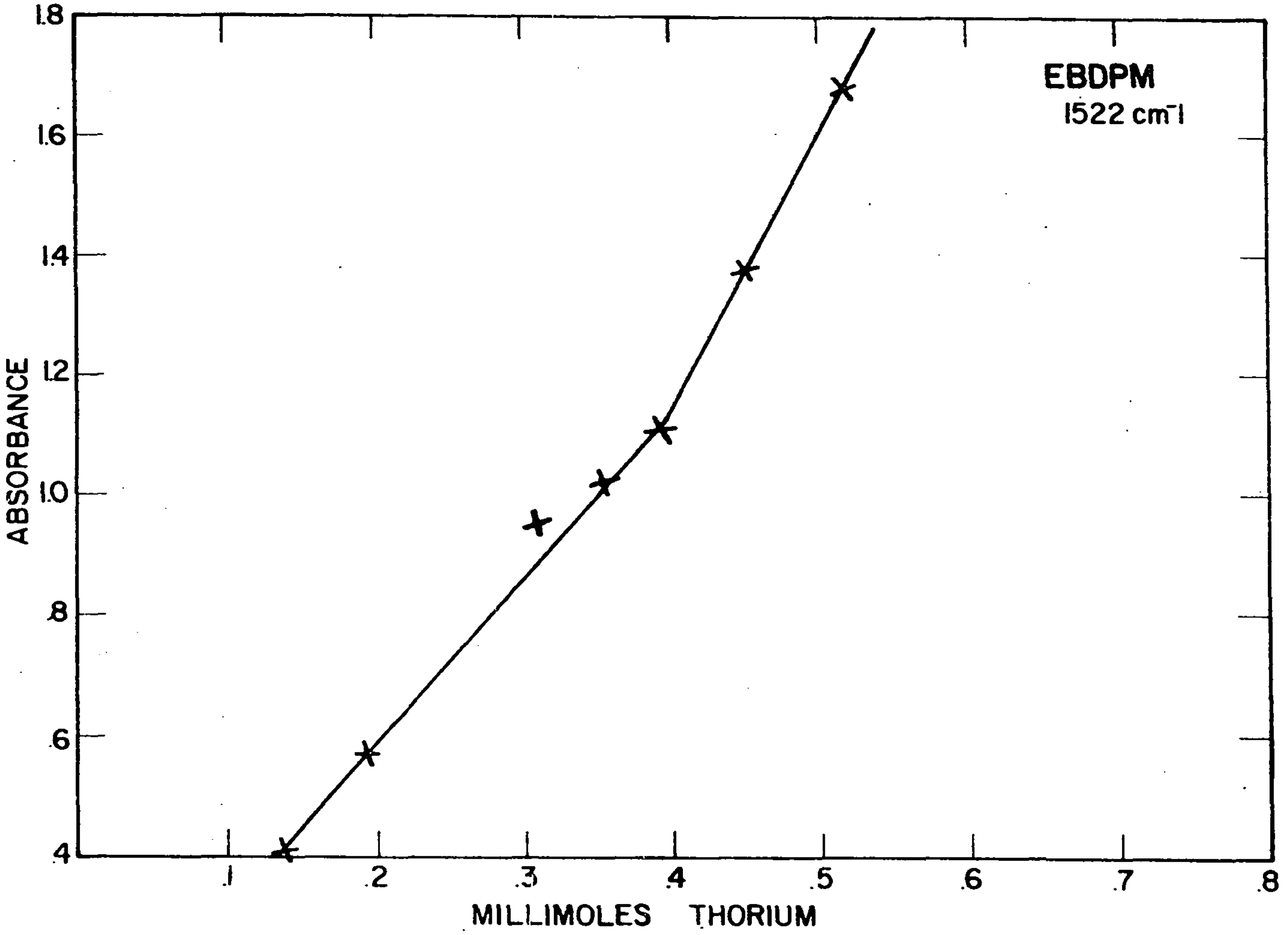


Figure 20. Absorbance of a v_4 covalent nitrate band as a function of thorium nitrate content

Table 35. Infrared bands of $Th(NO_3)_4 \cdot xEBDPM$ complexes

Band (cm^{-1})	Assignment
1170	free phosphoryl
1150	complex
1100	complex
1075	complex or ligand
1522	ν_4 covalent nitrate
1279	ν_1 covalent nitrate
1026	ν_2 covalent nitrate
1357	ν_3 ionic nitrate

<u>TOPO</u> The infrared spectra show the existence of two complexes with quite different nitrate bonding in each complex. The plots of the absorption of the nitrate bands versus the amount of thorium nitrate show either maxima or minima at a ligand:metal ratio of 3:1. The slope of the plot for one complex band has a break at a 3:1 ratio while the other does not have a break and is a straight line plot. This information coupled with the fact that thorium nitrate saturates TOPO at a 2:1 ligand:metal ratio leads to the conclusion that the two complexes are $Th(NO_3)_4 \cdot 2TOPO$ and $Th(NO_3)_4 \cdot 3TOPO$. A list of some of the infrared bands present is given in Tables 36 and 37. The plots of the absorbances of the bands versus thorium nitrate content. No evidence was found for the exis-

Table 36. Infrared bands of $Th(NO_3)_4 \cdot 2TOPO$

Band (cm^{-1})	Assignment
1170	free phosphoryl
1084	complex
1562	ν_4 covalent nitrate
1536	ν_4 covalent nitrate
1278	ν_1 covalent nitrate
1018	ν_2 covalent nitrate

Table 37. Infrared bands of $Th(NO_3)_4 \cdot 3TOPO$

Band (cm^{-1})	Assignment
1170	free phosphoryl
1106	complex
1500	ν_4 covalent nitrate
1303	ν_1 covalent nitrate
1030	ν_2 covalent nitrate

tence of any ionic nitrate in these complexes either when carbon tetrachloride or when 1,2-dichloroethane was used as a solvent.

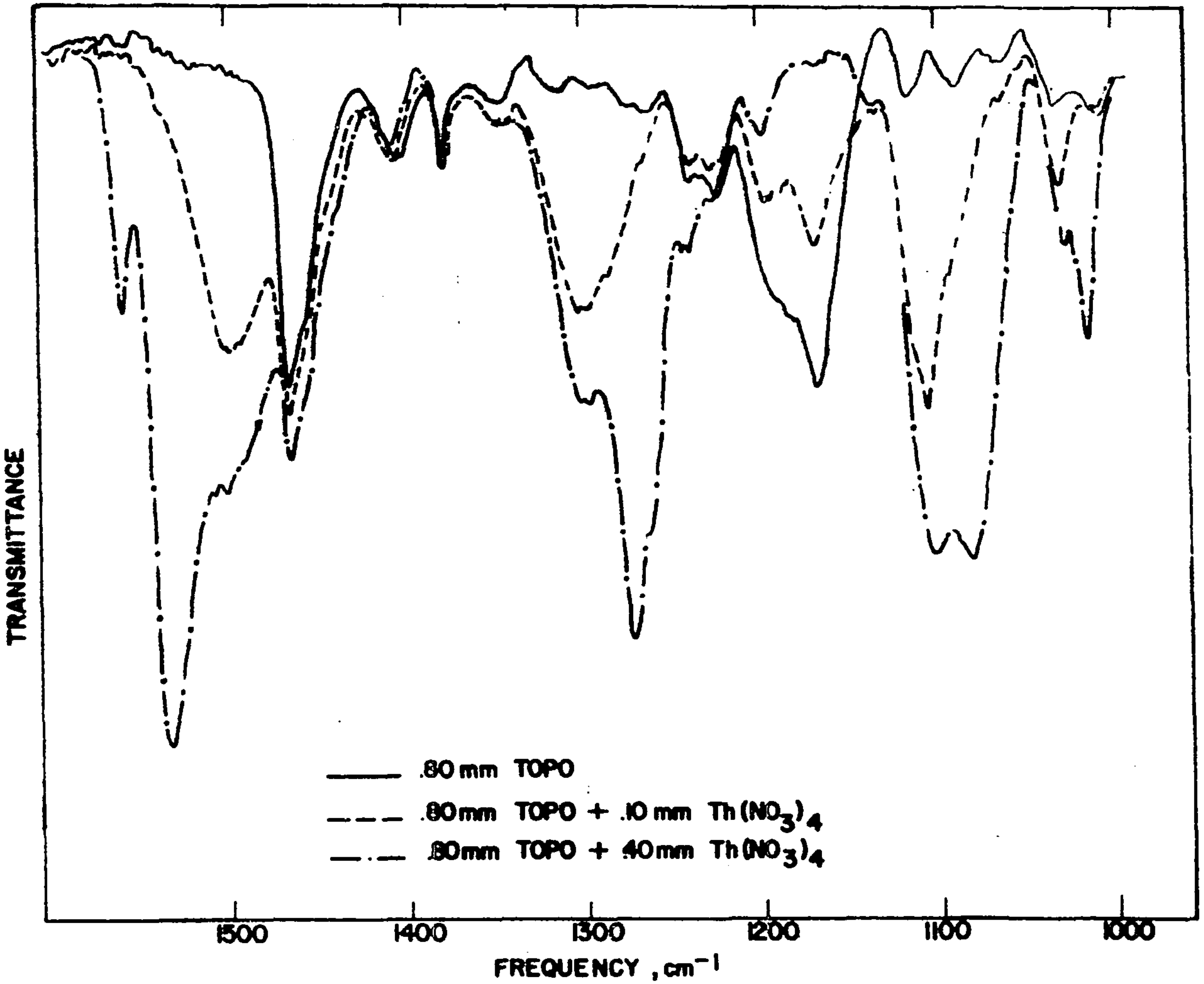


Figure 21. Infrared spectra of the TOPO-$Th(NO_3)_4$ system

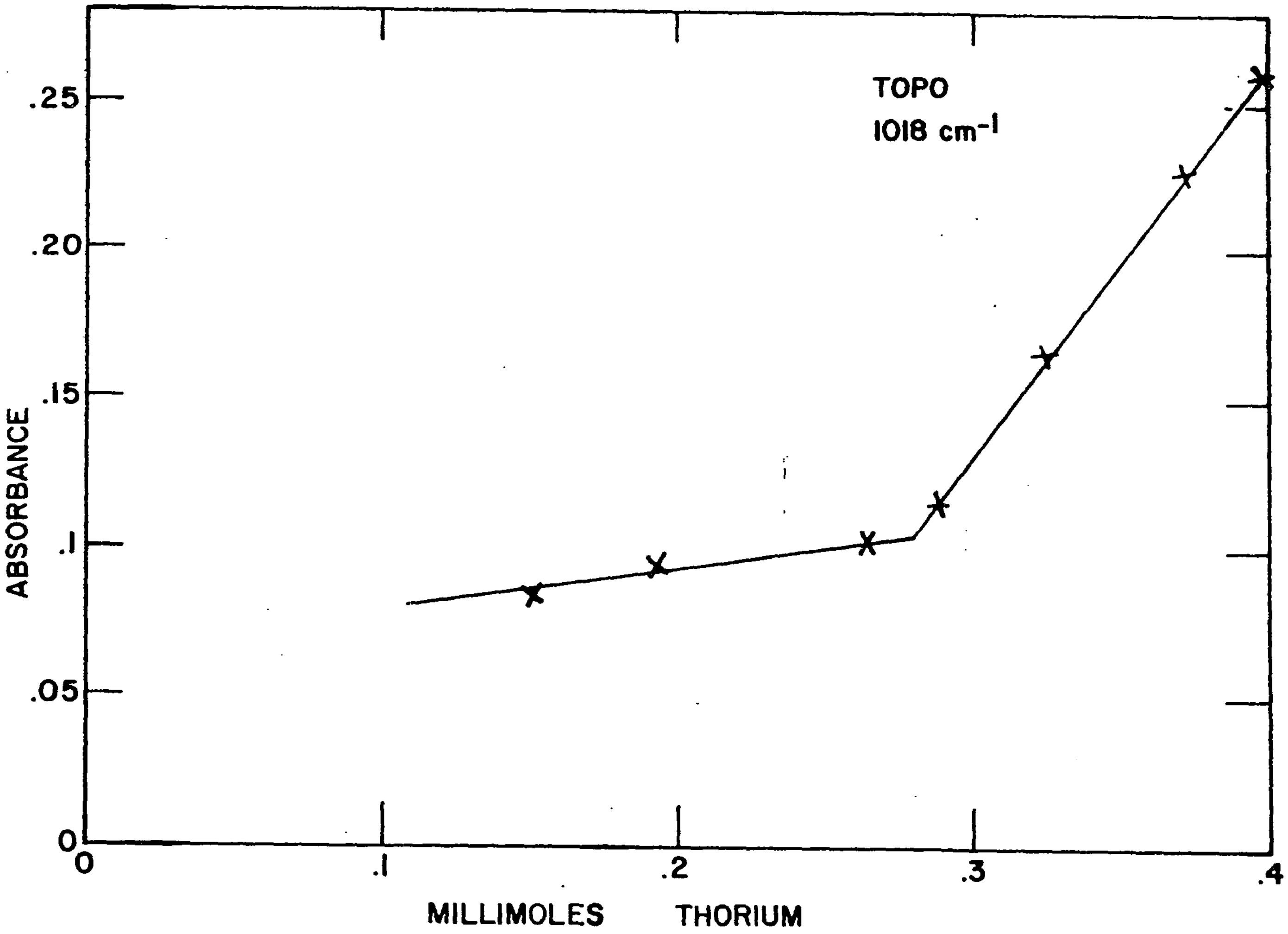
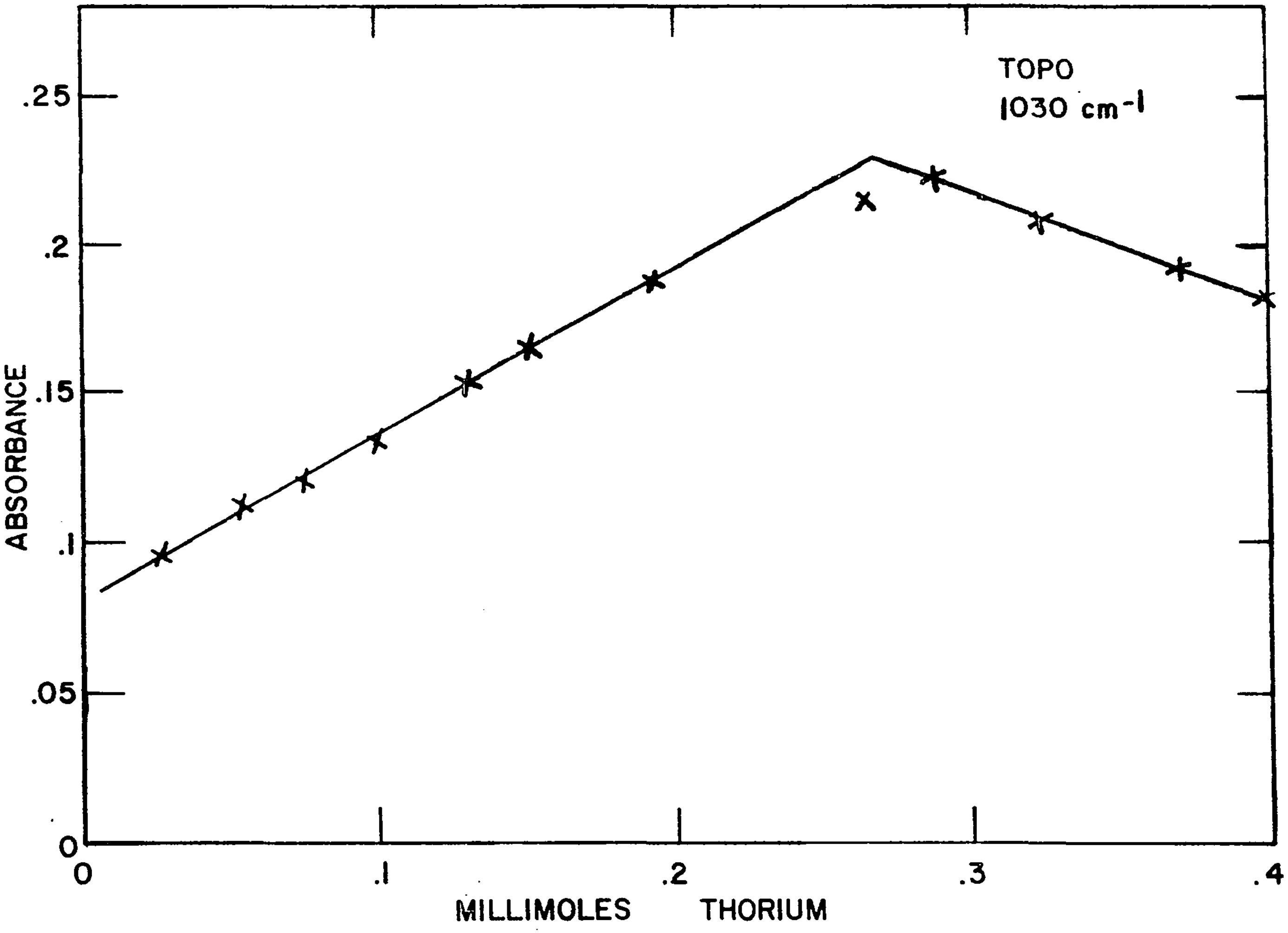


Figure 22. Absorbance of a ν_2 covalent nitrate band as a function of thorium nitrate content

Figure 23. Absorbance of a ν_2 covalent nitrate band as a function of thorium nitrate content


TOPO
1030 cm-1
ABSORBANCE
.25
.2
.15
.1
.05
0
0
.1
.2
.3
.4
MILLIMOLES THORIUM

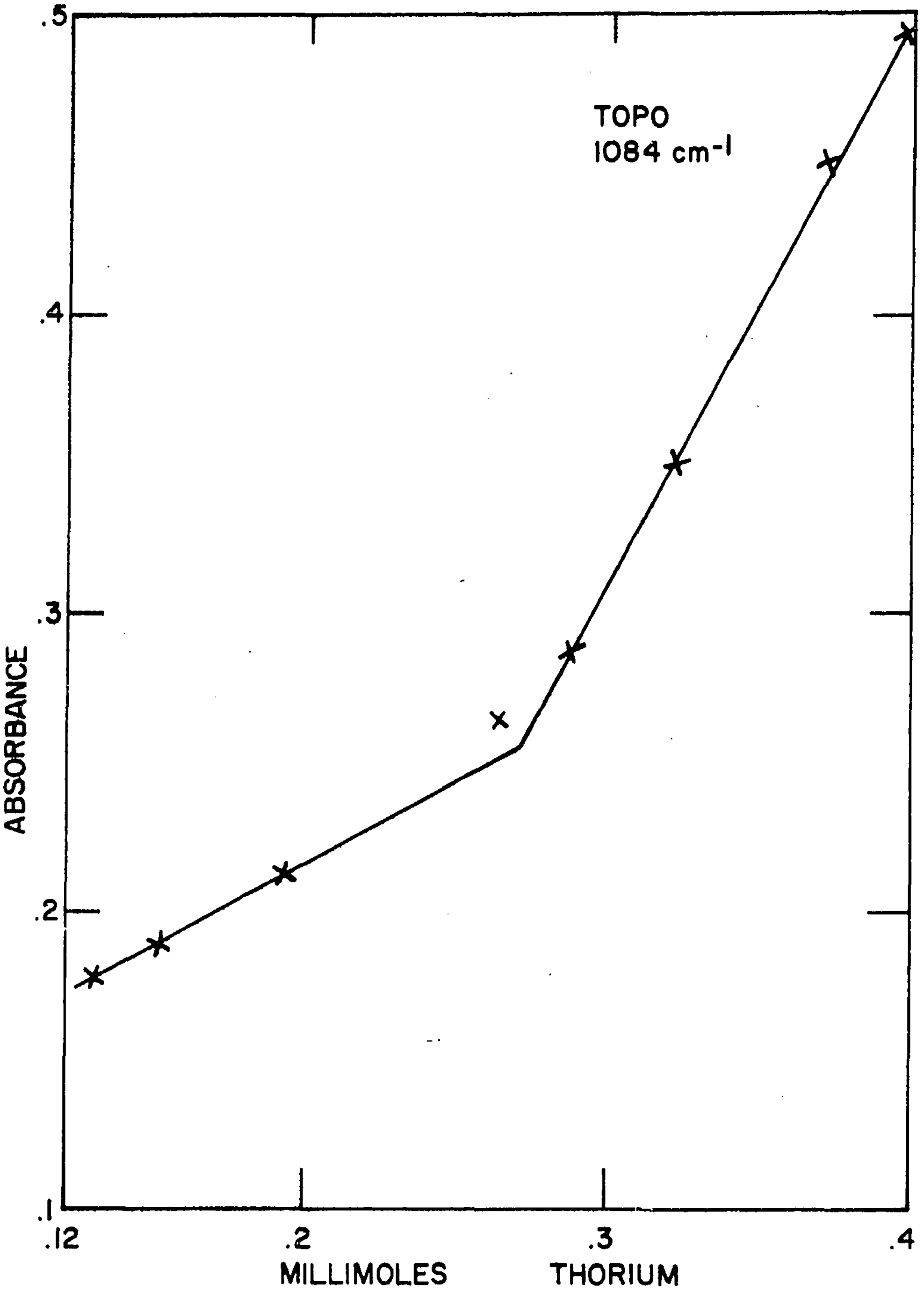


Figure 24. Absorbance of a complex band as a function of thorium nitrate content

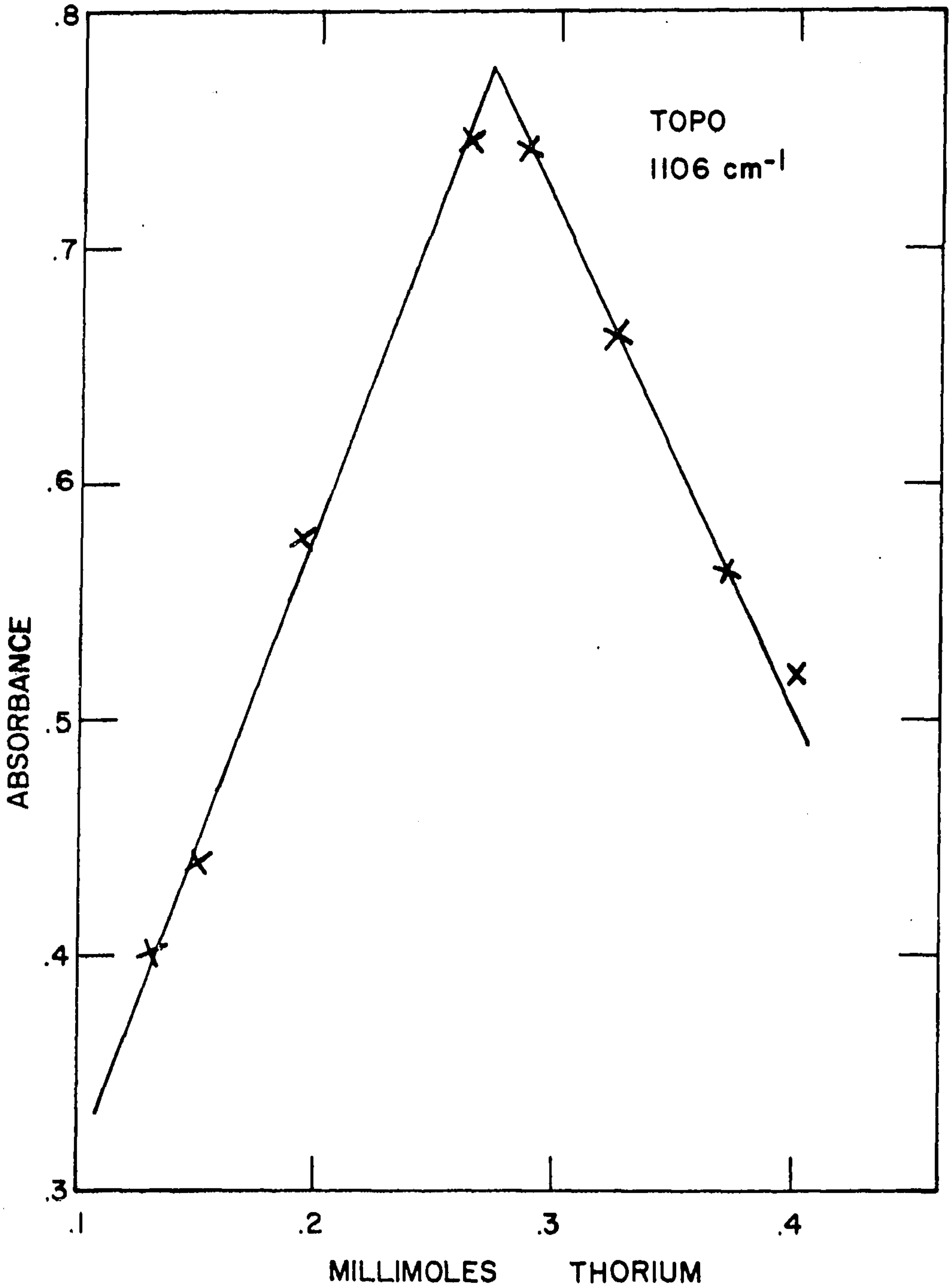


Figure 25. Absorbance of a complex band as a function of thorium nitrate content

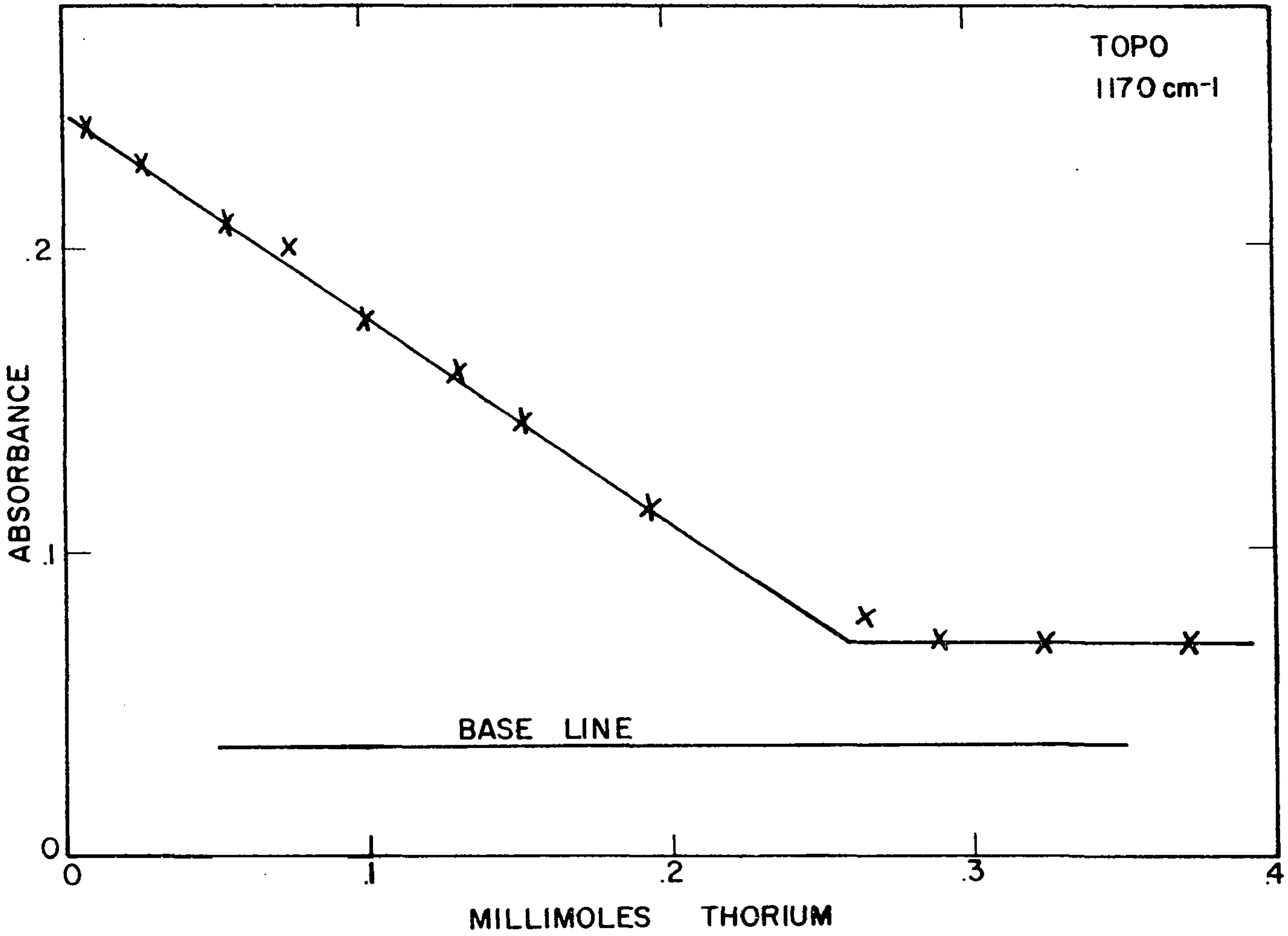
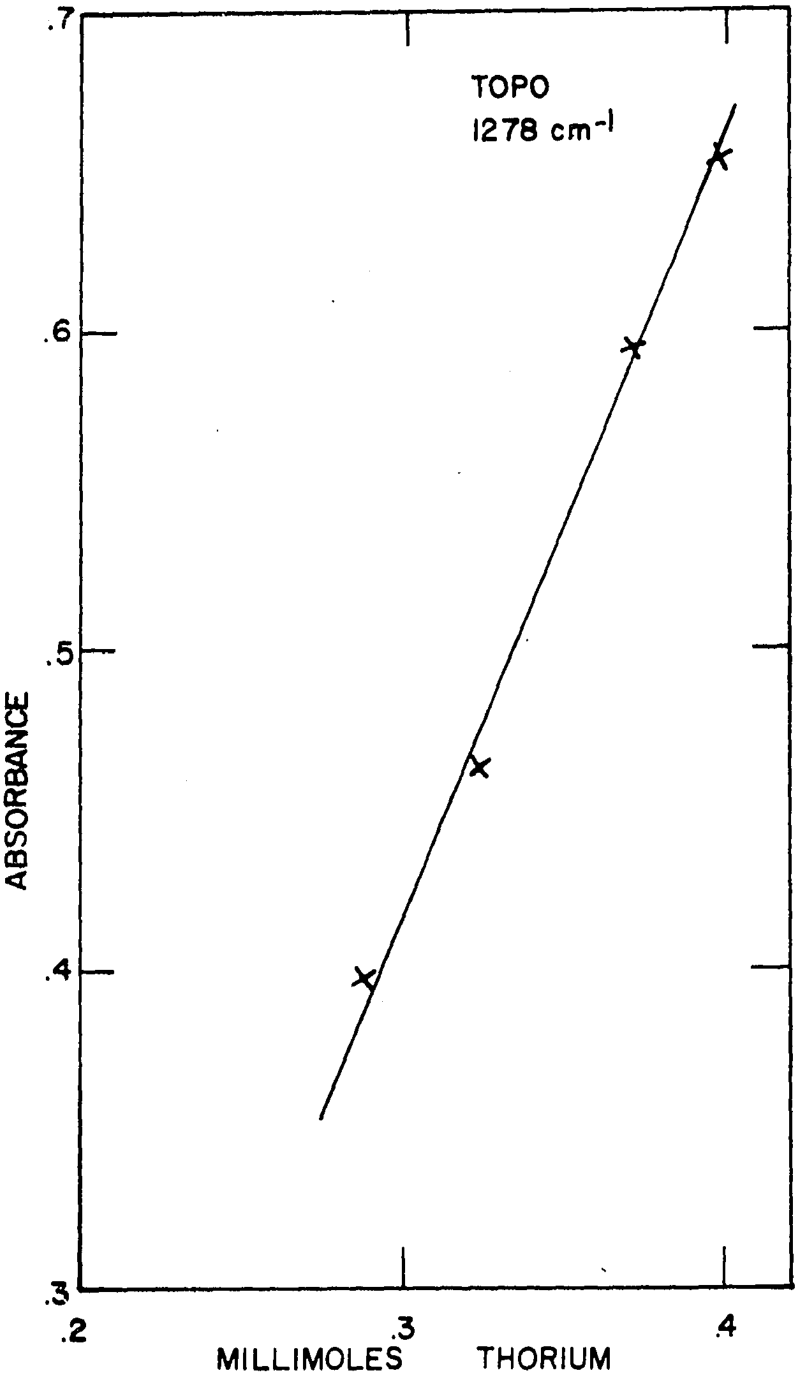


Figure 26. Absorbance of the free phosphoryl band as a function of thorium nitrate content

Figure 27. Absorbance of a ν_1 covalent nitrate band as a function of thorium nitrate content


TOPO
1278 cm⁻¹
ABSORBANCE
.7
.6
.5
.4
.3
.2
.3
.4
MILLIMOLES THORIUM

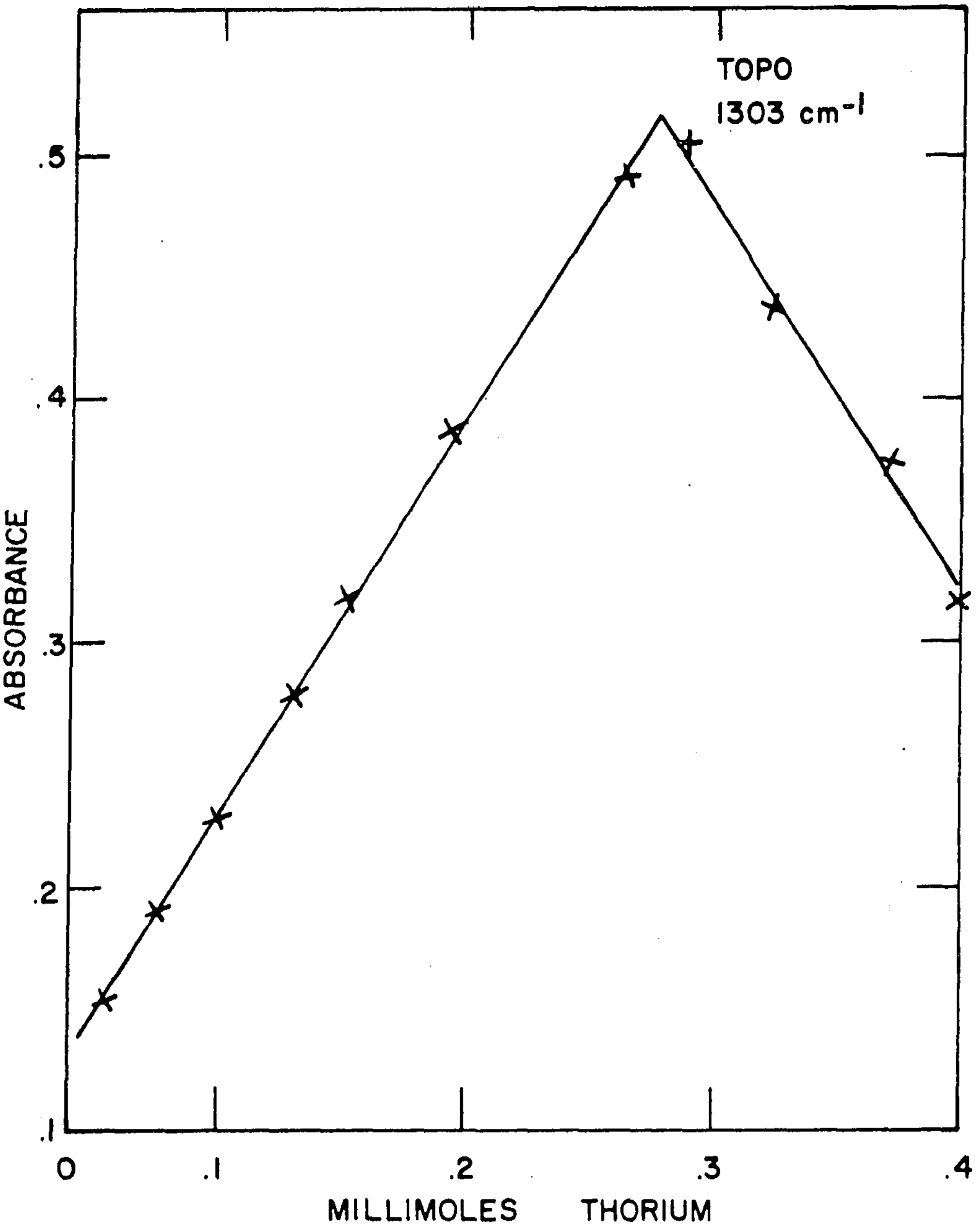


Figure 28. Absorbance of a ν_1 covalent nitrate band as a function of thorium nitrate content

Figure 29. Absorbance of a ν_4 covalent nitrate band as a function of thorium nitrate content

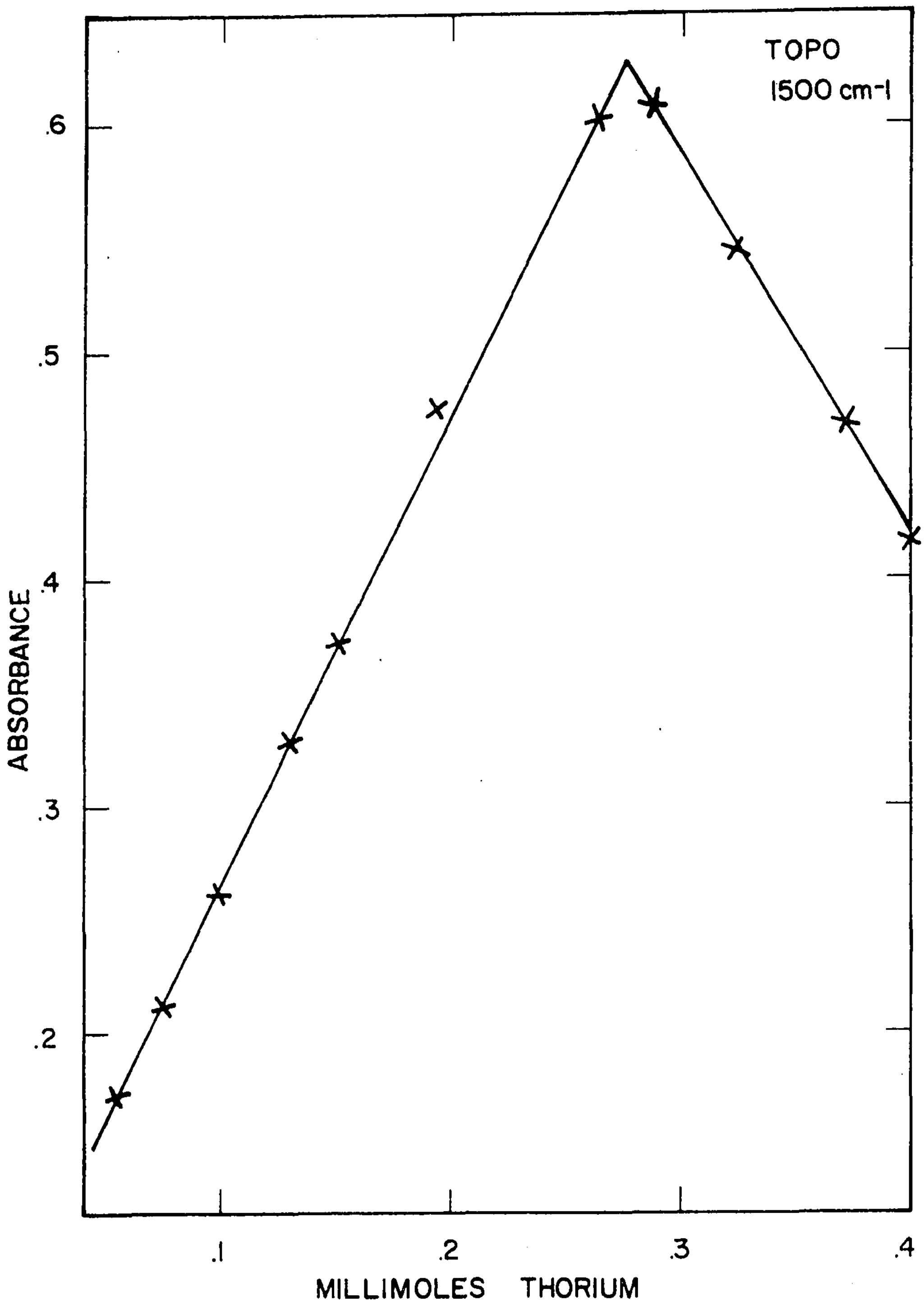

TOPO
1500 cm-1
ABSORBANCE
.6
.5
.4
.3
.2
.1
.2
.3
.4
MILLIMOLES THORIUM

Figure 30. Absorbance of a v_4 covalent nitrate band as a function of thorium nitrate content

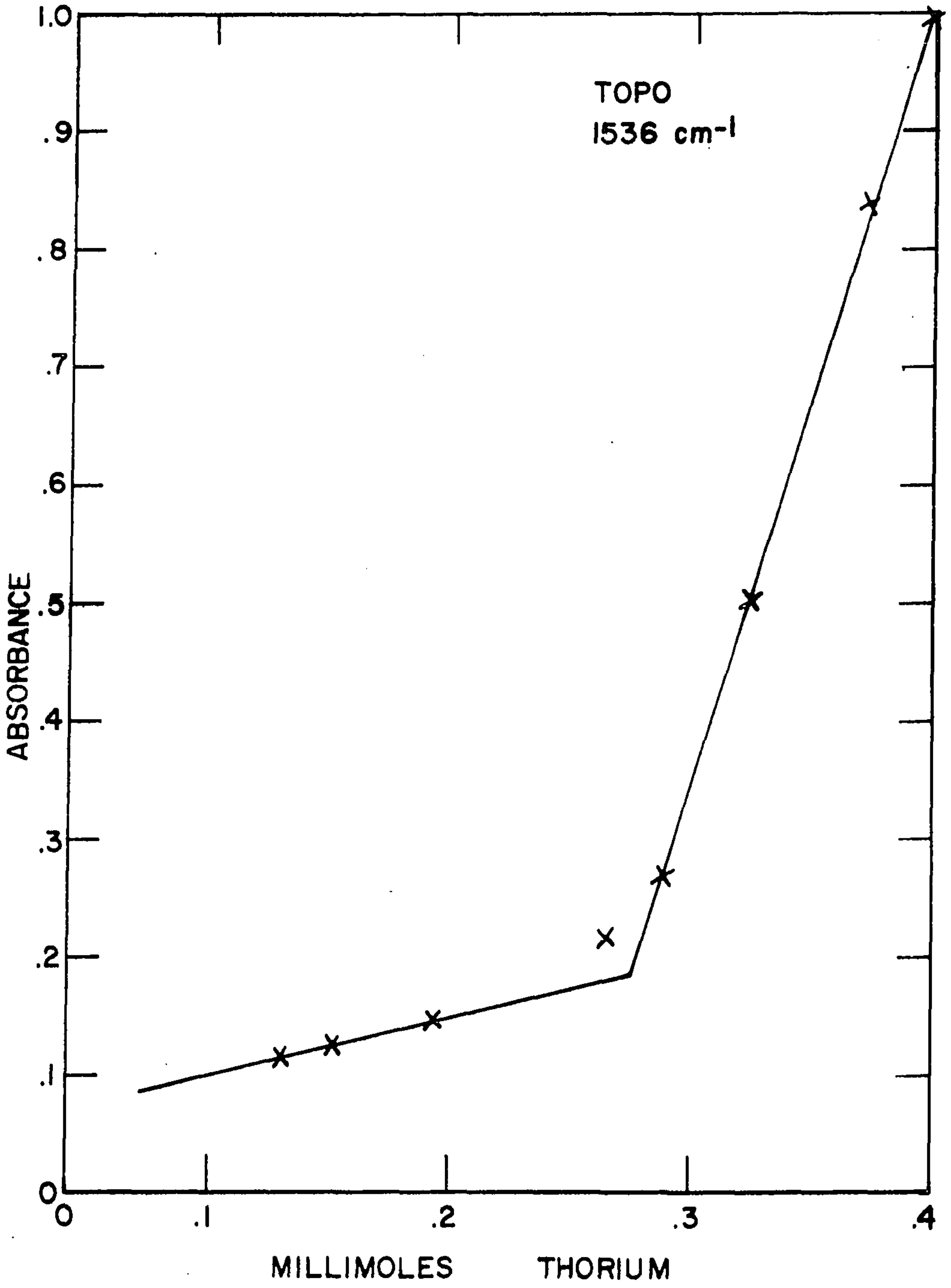
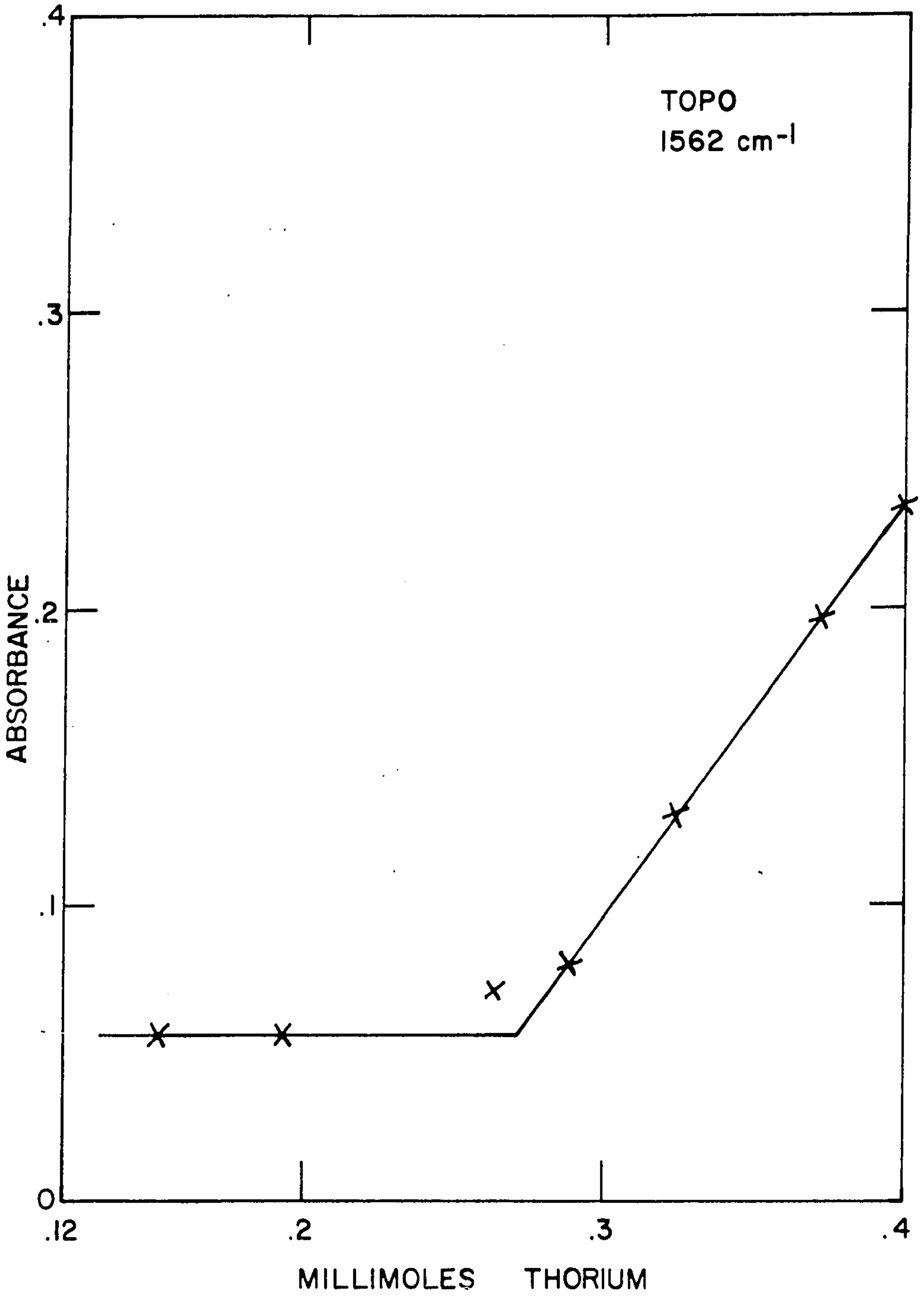

TOPO
1536 cm-1
ABSORBANCE
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
.1
.2
.3
.4
MILLIMOLES THORIUM

Figure 31. Absorbance of a ν_4 covalent nitrate band as a function of thorium nitrate content


TOPO
1562 cm-1
ABSORBANCE
.4
.3
.2
.1
0
.12
.2
.3
.4
MILLIMOLES THORIUM

TEHPO The most intensely absorbing band for the TEHPO-Th$(NO_3)_4$ system is at 1066 cm^{-1}. The plot of the absorbance of this band versus the amount of thorium nitrate shows a small break in slope at a ligand:metal ratio of 2.8:1 and continues to increase in intensity until saturation. These data coupled with the saturation data indicate that two complexes are formed, with ligand:metal ratios of 3:1 and 2:1. Bands at 1085 cm^{-1} and 1115 cm^{-1} may be complex bands or else absorption bands of the free ligand on the side of the 1066 cm^{-1} complex band. The plots for the nitrate bands show no breaks in the slopes. Evidently, the nitrate bonding is the same in all the complexes formed. A list of some of the infrared bands is given in Table 38. The plots of the absorbances of the bands versus thorium nitrate content are shown in Figures 33-40.

Table 38. Infrared bands of Th$(NO_3)_4 \cdot$xTEHPO complexes

Band (cm^{-1})	Assignment
1170	free phosphoryl
1115	complex or ligand
1085	complex or ligand
1066	complex
1563	v_4 covalent nitrate
1539	v_4 covalent nitrate
1275	v_1 covalent nitrate
1018	v_2 covalent nitrate

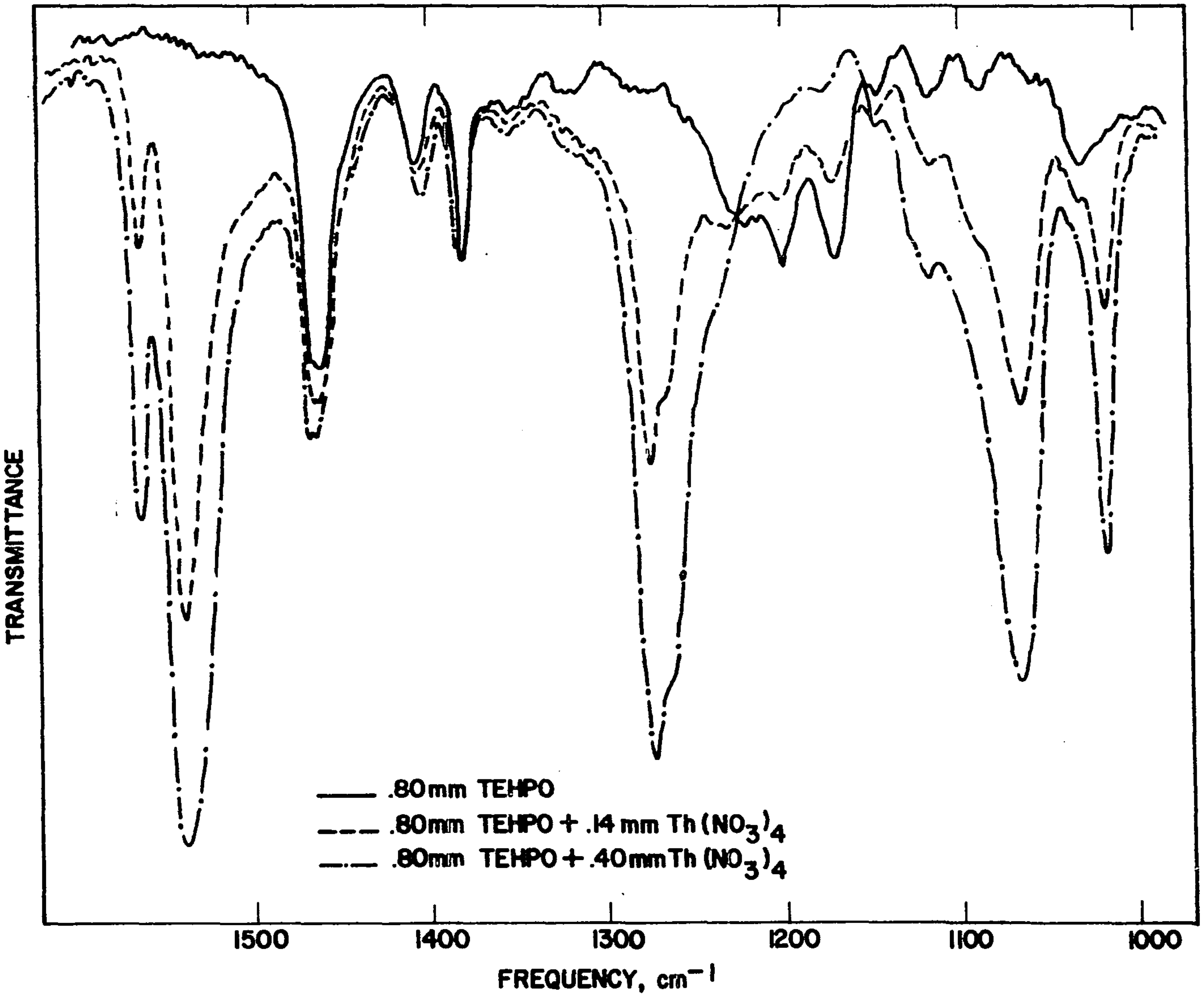


Figure 32. Infrared spectra of the TEHPO-Th(NO$_3$)$_4$ system

Figure 33. Absorbance of the ν_2 covalent nitrate band as a function of thorium nitrate content

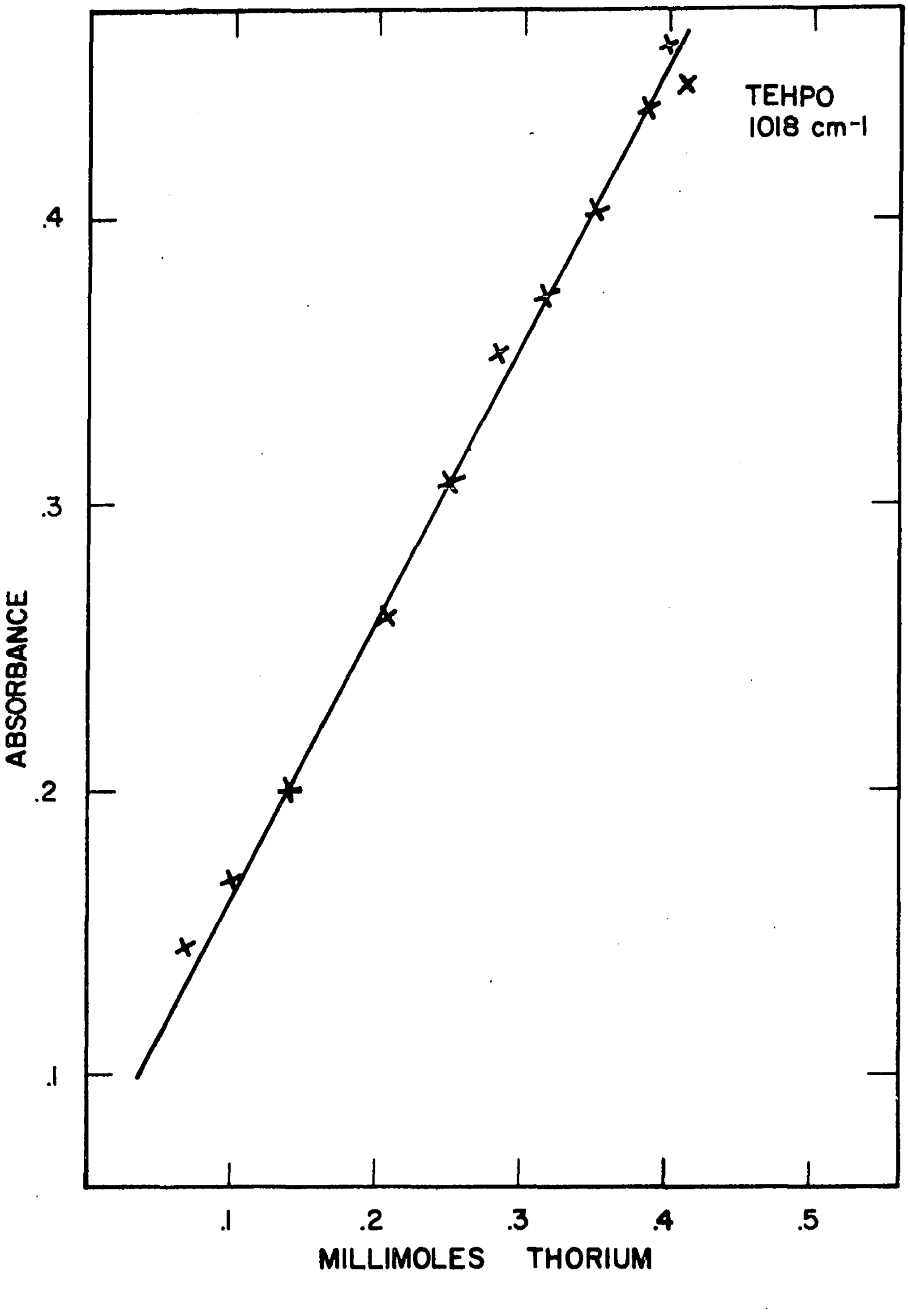

TEHPO
1018 cm-1
ABSORBANCE
.1
.2
.3
.4
.1
.2
.3
.4
.5
MILLIMOLES THORIUM

Figure 34. Absorbance of a complex band as a function of thorium nitrate content

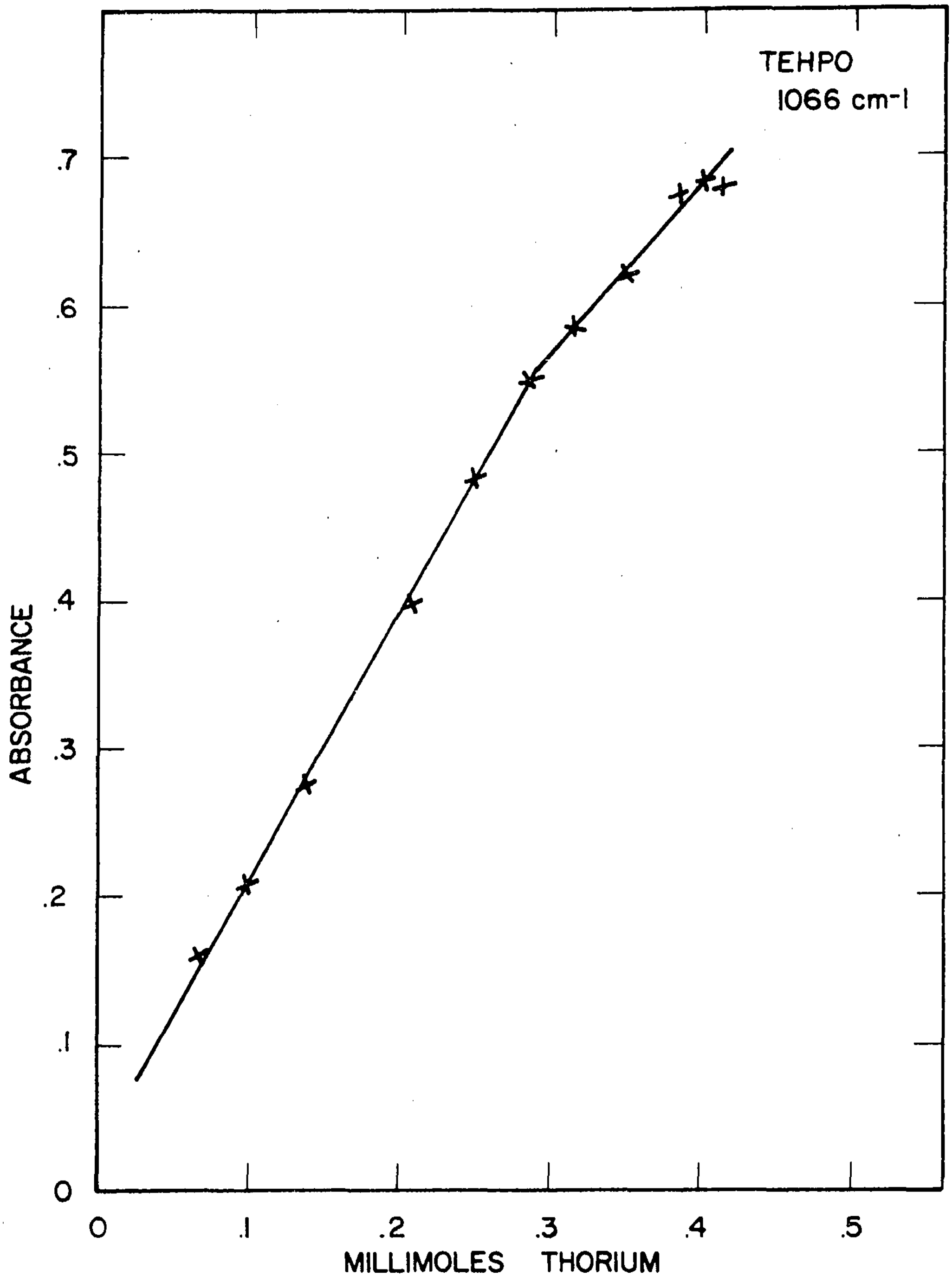
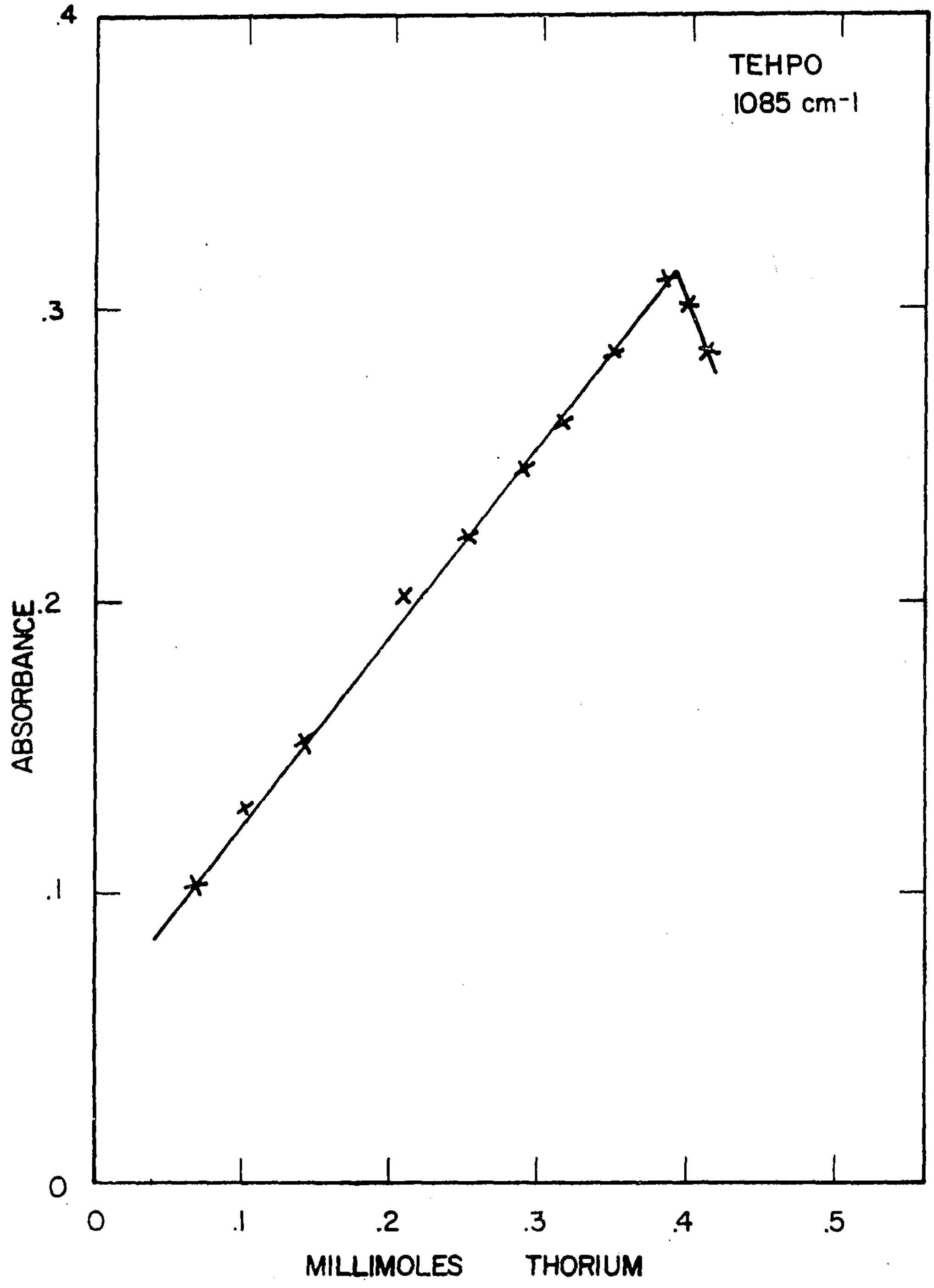

TEHPO
1066 cm-1
ABSORBANCE
0
.1
.2
.3
.4
.5
.6
.7
0
.1
.2
.3
.4
.5
MILLIMOLES THORIUM

Figure 35. Absorbance of a complex band as a function of thorium nitrate content


TEHPO
1085 cm-1
ABSORBANCE
.4
.3
.2
.1
0
0
.1
.2
.3
.4
.5
MILLIMOLES THORIUM

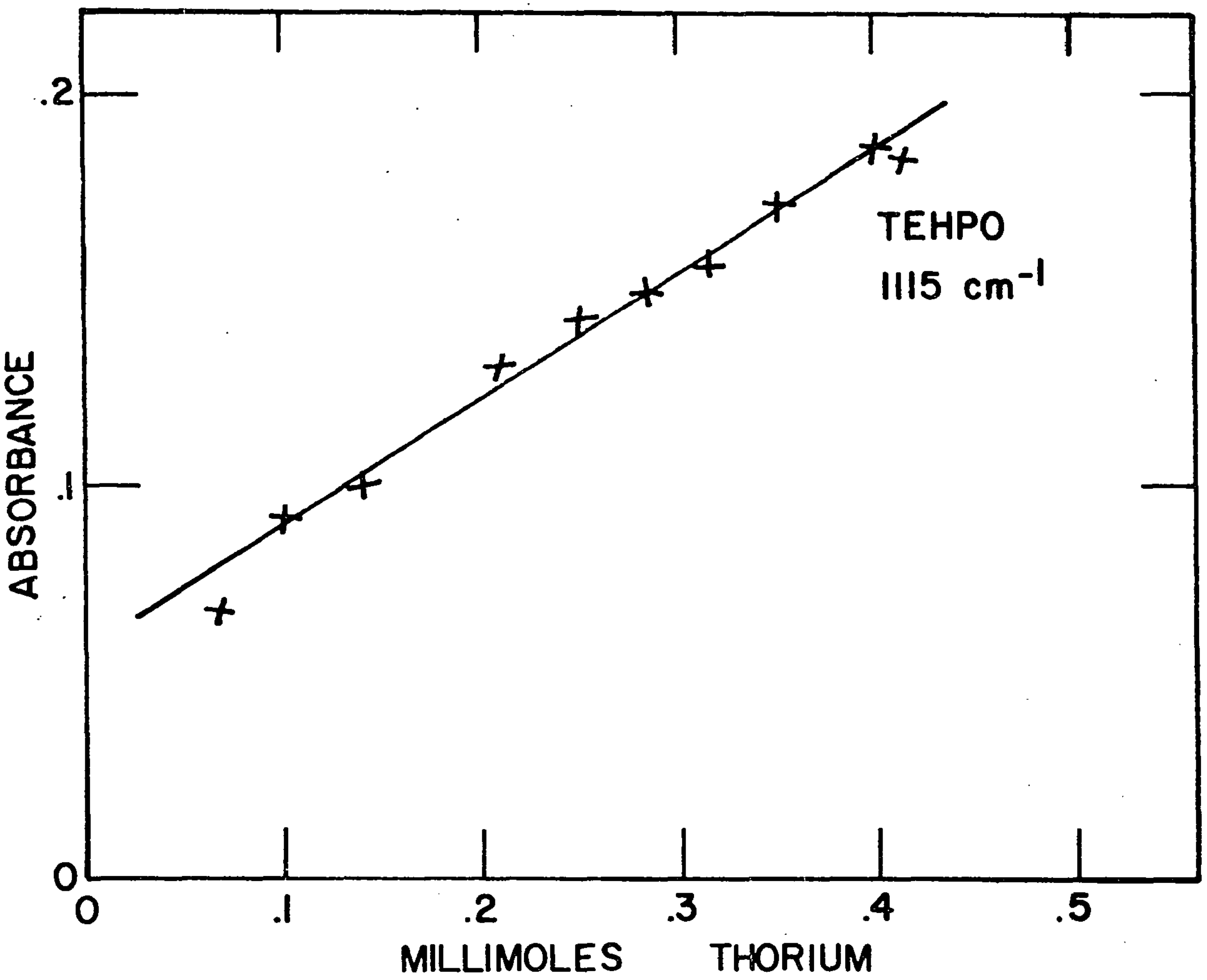


Figure 36. Absorbance of a complex band as a function of thorium nitrate content

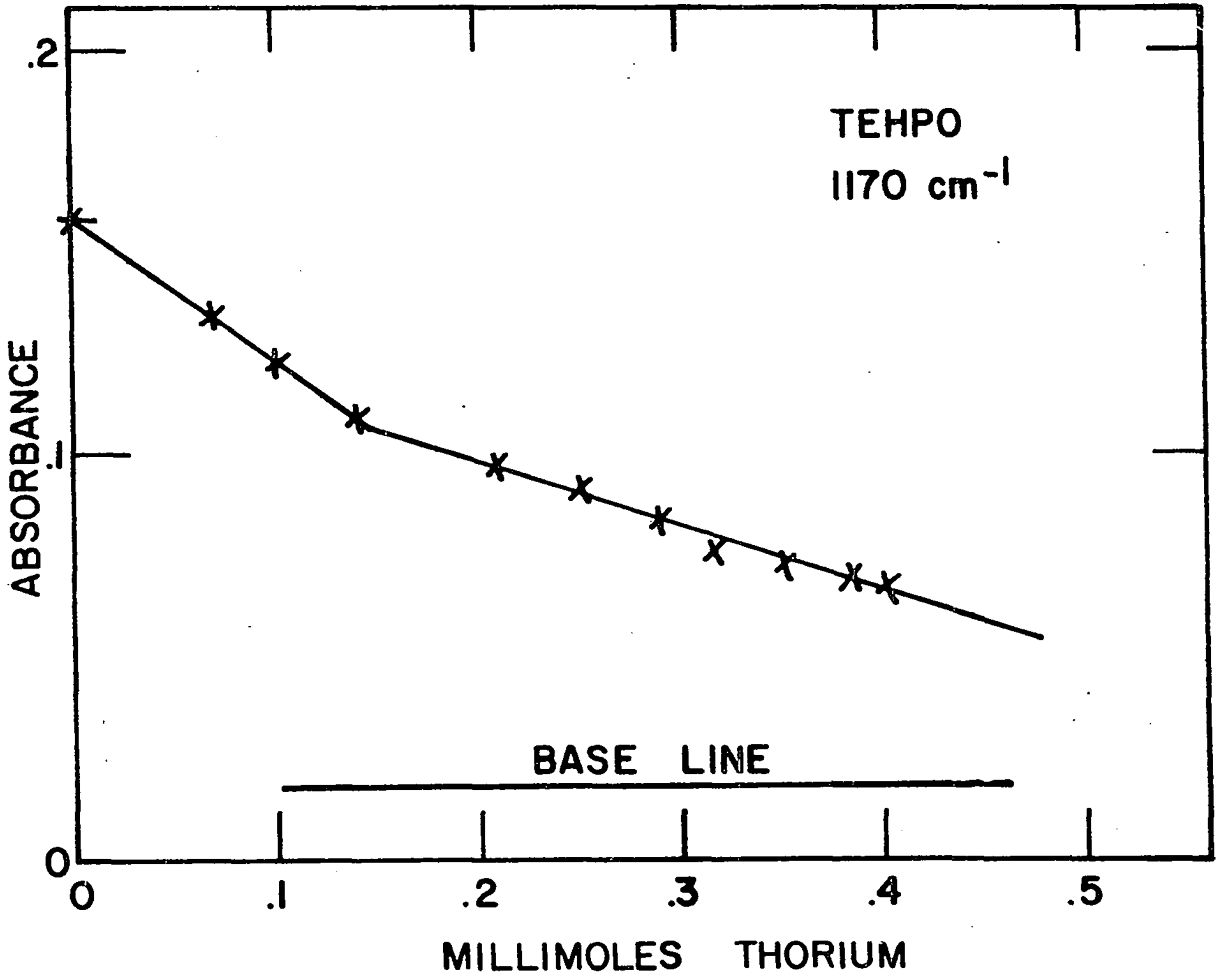


Figure 37. Absorbance of the free phosphoryl band as a function of thorium nitrate content

Figure 38. Absorbance of the ν_1 covalent nitrate band as a function of thorium nitrate content

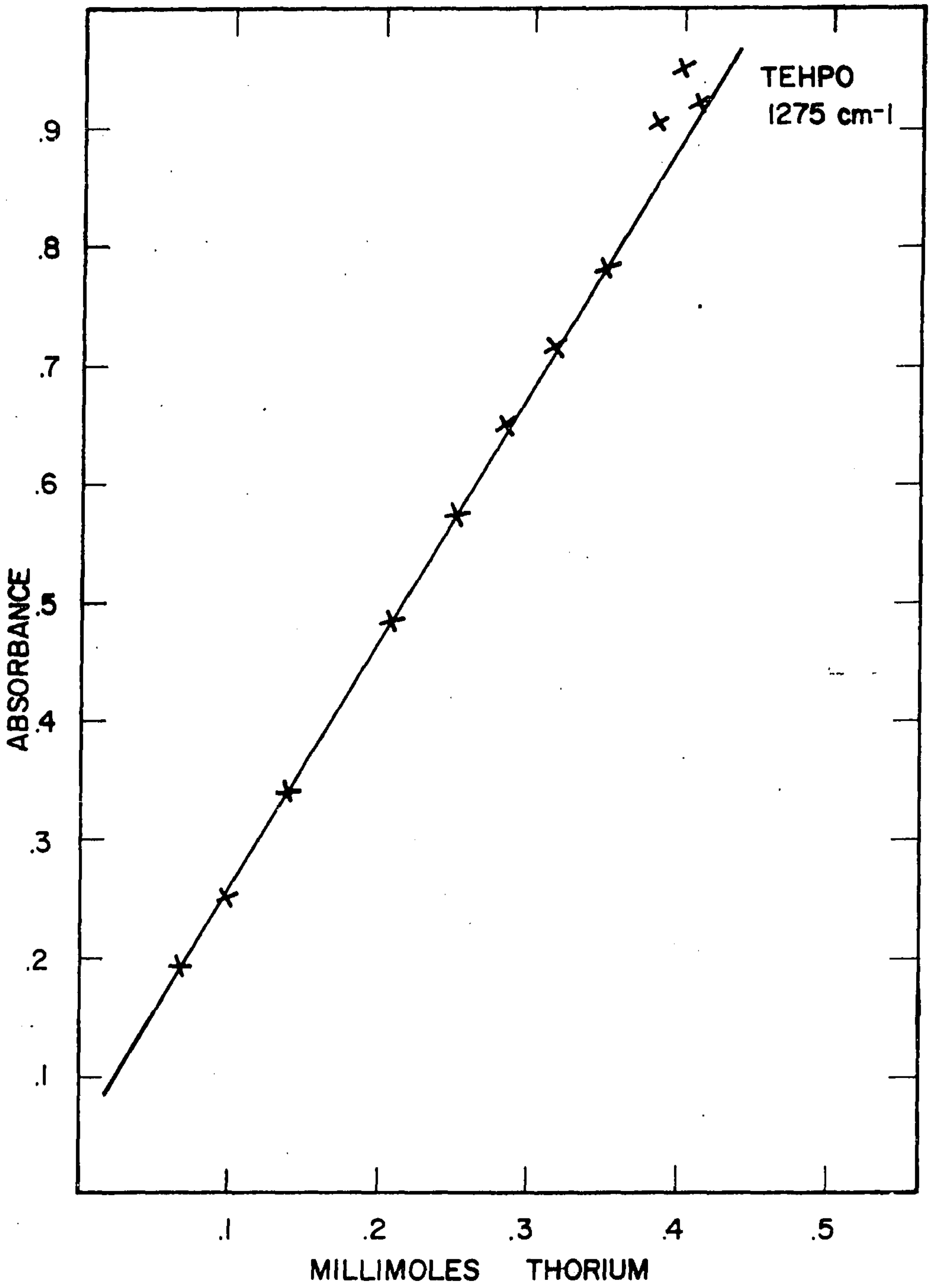

TEHPO
1275 cm-1
ABSORBANCE
.1
.2
.3
.4
.5
.6
.7
.8
.9
MILLIMOLES THORIUM
.1
.2
.3
.4
.5

Figure 39. Absorbance of a ν_4 covalent nitrate band as a function of thorium nitrate content

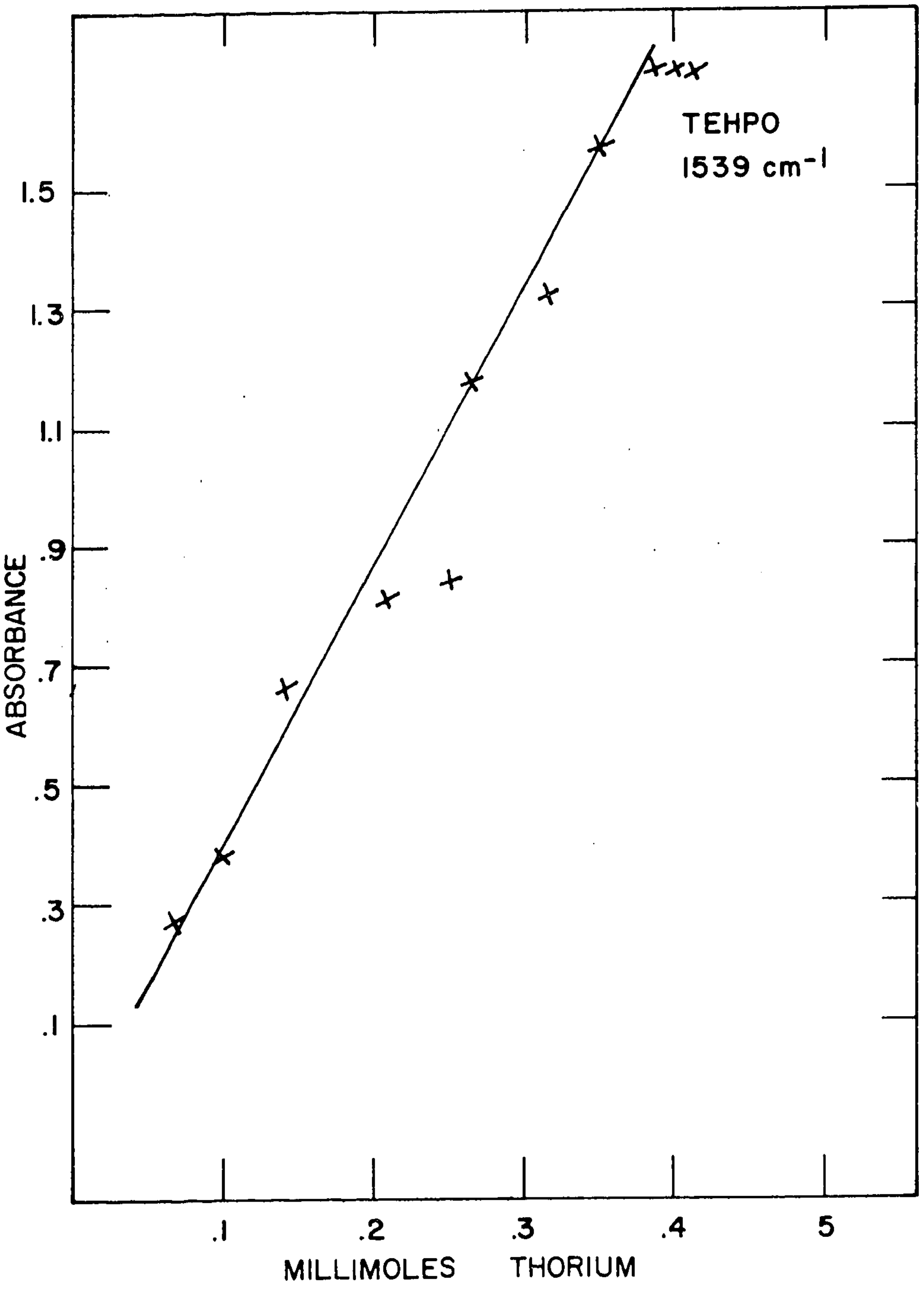
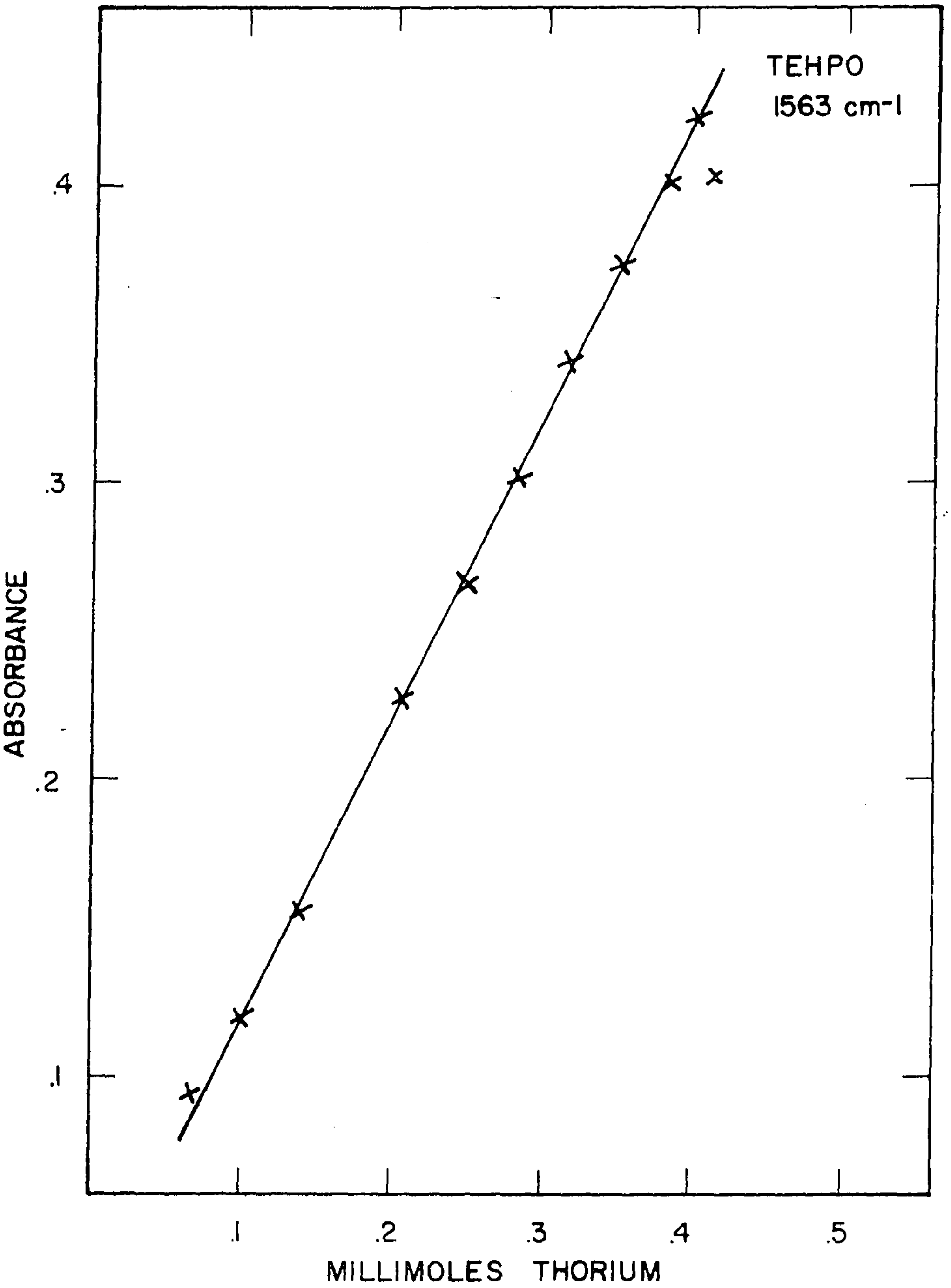

TEHPO
1539 cm^{-1}
ABSORBANCE
1.5
1.3
1.1
.9
.7
.5
.3
.1
.1
.2
.3
.4
5
MILLIMOLES THORIUM

Figure 40. Absorbance of a ν_4 covalent nitrate band as a function of thorium nitrate content


TEHPO
1563 cm-1
ABSORBANCE
.1
.2
.3
.4
.1
.2
.3
.4
.5
MILLIMOLES THORIUM

There is no evidence for the presence of any ionic nitrate. The 1018 cm^{-1} nitrate band has a shoulder at high ligand:metal ratios caused by an absorption band of the ligand. The 1275 cm^{-1} nitrate band has a shoulder indicating the presence of another nitrate band.

Equilibrium Studies on the Nature of the Extractable Species with Thorium Nitrate and Various Ligands

The extraction of thorium nitrate by a ligand (L) can be represented by the equation:

$$Th^{4+}_{(a)} + 4NO^{-}_{3(a)} + nL_{(o)} \rightleftarrows Th(NO_3)_4\cdot nL_{(o)}$$

$$k = \frac{[Th(NO_3)_4\cdot nL]\gamma_c}{\beta[Th^{4+}][NO_3^-]\ \gamma_{\pm}^5[L]^n\ \gamma_L^n} \qquad (1)$$

The symbols γ_c, γ_L, and $\gamma_{\pm}$ are the activity coefficients of the extracted complex, the extractant, and the mean activity coefficient for thorium nitrate in the aqueous phase; β is the fraction of the thorium in the aqueous phase that is uncomplexed by nitrate. The equilibrium expression in Equation 1 can be rearranged as shown in Equation 2.

$$K' = \frac{K\ \gamma_{\pm}^5\ \gamma_L^n\ \beta}{\gamma_c} = \frac{D}{[L]^n\ [NO_3^-]^4} \qquad (2)$$

This equation shows that if the activity coefficients and the nitrate ion concentration are constant, then for a series of extractions the slope of a plot of log D versus log [L] will give n. If the nitrate ion concentration is not constant then $\log \frac{D}{[NO_3^-]^4}$ should be plotted against log [L]. D is determined by measuring the concentration of thorium in one of the phases and from a knowledge of total thorium. D is defined as the ratio of the concentration of thorium in the organic phase to its concentration in the aqueous phase. The concentration of free ligand, [L], is determined from a knowledge of the total concentration of ligand and the concentration of thorium in the organic phase as shown in Equation 3.

$$[L] = [L]_{total} - n\ [Th(NO_3)_4 \cdot nL] \qquad (3)$$

This means of course that n must be estimated until the value chosen agrees with the slope obtained from a plot of log D versus log [L]. In actual practice it was found that when the initial concentration of ligand was in excess of the initial concentration of metal a wrong guessed value for n caused only a small error in the slope.

Equilibrium studies were made using constant initial concentrations of thorium nitrate and varying initial concentrations of ligand. The ligands used were HDPM, EBDPM, TOPO, and TEHPO. Using excess extractant the "slope plots" as shown in Figures 41, 44-46 indicate the extraction of $Th(NO_3)_4 \cdot 2HDPM$, $Th(NO_3)_4 \cdot 2EBDPM$, $Th(NO_3)_4 \cdot 3TOPO$, and $Th(NO_3)_4 \cdot 3TEHPO$. When excess metal is used, the species extracted as interpreted from Figures 42 and 43 are

$Th(NO_3)_4 \cdot HDPM$ and $Th(NO_3)_4 \cdot EBDPM$. However, whenever excess metal is used the concentration of free ligand is very small and because it is being determined indirectly the results cannot be considered very accurate.

Previous infrared data indicated that a complex $Th(NO_3)_4 \cdot 3HDPM$ might be the cause of the appearance of an ionic nitrate band. Equilibrium studies were carried out using as high ligand:metal ratios as possible which would leave amounts of thorium in the aqueous phase detectable by arsenazo III. The plot of log D versus log [L] gave a slope of 2.3. This is not convincing evidence for the existence of a 3:1 complex.

Table 39. The extraction of $Th(NO_3)_4 \cdot 2HDPM$[a]

$[HDPM]_i \times 10^3$	D	$K' \times 10^{-9}$
4.00	1.987	5.03
5.00	3.410	4.80
7.00	10.77	5.90
8.00	16.36	5.98
8.00	16.15	5.89
10.00	28.56	5.40
15.00	76.16	4.84
4.00	1.993	5.06
5.00	3.437	4.86
7.00	10.58	5.79
10.00	29.20	5.53
15.00	85.83	5.46
		av. 5.38±.38

[a] Conditions: solvent = 1,2-dichlorobenzene; $[Th(NO_3)_4]_i$ = 0.001667 M; $[HNO_3]_i$ = 0.1034 M.

Table 40. The extraction of $Th(NO_3)_4 \cdot HDPM^a$

$[HDPM]_i \times 10^4$	$D \times 10^2$	$K' \times 10^{-2}$
50.00	2.804	5.22
50.00	2.793	5.18
100.0	5.450	5.29
100.0	5.400	5.17
50.00	2.748	5.00
50.00	2.743	4.98
100.0	5.570	5.54
100.0	5.654	5.74
20.00	1.078	4.56
40.00	2.165	4.75
3.480	0.1762	3.91
4.982	0.2491	3.81
10.13	0.5176	4.01
49.97	2.786	5.15
		av. 4.88±.48

[a] Conditions: solvent = 1,2-dichlorobenzene; $[Th(NO_3)_4]_i$ = 0.1000 M; $[HNO_3]_i$ = 0.00300 M.

Table 41. The extraction of $Th(NO_3)_4 \cdot 2EBDPM^a$

$[EBDPM]_i \times 10^3$	D	$K' \times 10^{-8}$
8.544	1.422	3.16
12.12	3.219	3.53
17.76	7.481	3.45
25.28	19.06	3.93
34.14	52.27	4.38
		av. 3.68 ± .29

[a] Conditions: solvent = 1,2-dichlorobenzene; $[KNO_3]$ = 0.100 M; $[Th(NO_3)_4]_i$ = 0.002030 M; $[HNO_3]_i$ = 0.001 M.

Table 42. The extraction of $Th(NO_3)_4 \cdot EBDPM^a$

$[EBDPM]_i \times 10^4$	$D \times 10^3$	$K' \times 10^{-2}$
2.00	1.065	4.33
4.00	2.108	4.25
5.00	2.656	4.33
10.00	5.420	4.56
2.00	1.064	4.32
4.00	2.104	4.23
5.00	2.660	4.34
10.00	5.339	4.52
40.00	21.80	4.58
		av. 4.38 ± .11

[a] Conditions: solvent = 1,2-dichlorobenzene; $[Th(NO_3)_4]_i$ = 0.100 M; $[HNO_3]_i$ = 0.003 M.

Table 43. The extraction of $Th(NO_3)_4 \cdot 3TOPO^a$

$[TOPO]_i \times 10^2$	D	$K' \times 10^{-9}$
1.00	0.615	8.95
1.00	0.573	8.05
1.00	0.601	8.62
1.00	0.611	8.86
1.50	1.688	8.36
1.50	1.724	8.61
2.00	3.510	7.26
2.50	6.718	6.94
2.50	6.760	6.99
2.50	6.854	7.09
3.75	17.92	4.96
3.75	17.92	4.96
5.00	54.56	5.95
		av. 7.35 ± .89

[a] Conditions: solvent = 1,2-dichlorobenzene; $[Th(NO_3)_4]_i$ = 0.001667 M; $[HNO_3]_i$ = 0.1034 M.

Table 44. The extraction of $Th(NO_3)_4 \cdot 3TOPO$[a]

$[TOPO]_i \times 10^3$	D	$K' \times 10^{-10}$
3.00	31.54	2.14
3.50	51.88	2.02
4.00	75.92	1.85
4.50	125.9	2.05
6.00	234.6	1.44
6.00	227.7	1.40
7.50	665.3	1.95
7.50	707.3	2.08
		av. 1.87 ± .23

[a] Conditions: solvent = cyclohexane; $[KNO_3] = 0.100\ \underline{M}$; $[Th(NO_3)_4]_i = 0.002030\ \underline{M}$; $[HNO_3]_i = 0.001\ \underline{M}$.

Table 45. The extraction of $Th(NO_3)_4 \cdot 3TOPO$[a]

$[TOPO]_i \times 10^3$	D	$K' \times 10^{-7}$
12.50	0.641	3
5.00	0.170	3
2.50	0.079	9
0.500	0.0091	4
0.250	0.0038	9
		av. 5.6 ± 2.7

[a] Data from Zingaro and White (205); conditions: solvent = cyclohexane; $[Th(NO_3)_4]_i = 0.00957\ \underline{M}$; $[HNO_3]_i = 0.00983\ \underline{M}$; $[NaNO_3] = 2.0\ \underline{M}$.

Table 46. The extraction of $Th(NO_3)_4 \cdot 3TEHPO$[a]

$[TEHPO]_i \times 10^2$	D	$K' \times 10^{-4}$
2.50	0.5647	4.76
2.50	0.5720	4.83
3.50	1.395	4.51
3.50	1.367	4.61
4.50	3.041	4.61
4.50	2.991	4.54
3.00	0.9454	4.80
5.00	4.873	5.38
6.00	7.997	4.92
7.00	11.65	4.45
7.00	11.45	4.29
		av. 4.68 ± .20

[a] Conditions: solvent cyclohexane; $[Th(NO_3)_4]_i = 0.002030$ $\underline{M}$; $[HNO_3]_i = 0.001$ $\underline{M}$; $[KNO_3] = 1.000$ $\underline{M}$.

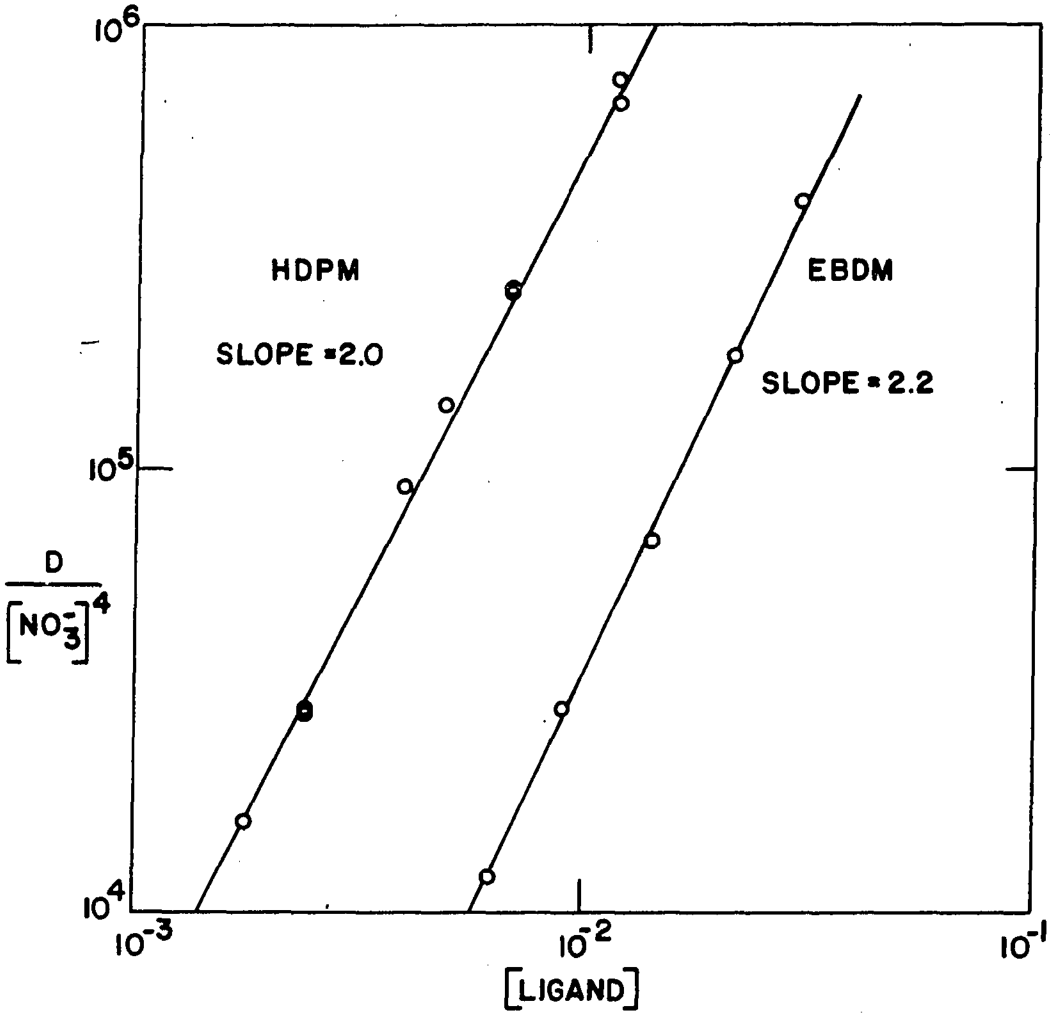


Figure 41. The extraction of $Th(NO_3)_4 \cdot 2HDPM$ and $Th(NO_3)_4 \cdot 2EBDPM$; solvent = 1,2-dichlorobenzene (see Tables 39 and 41)

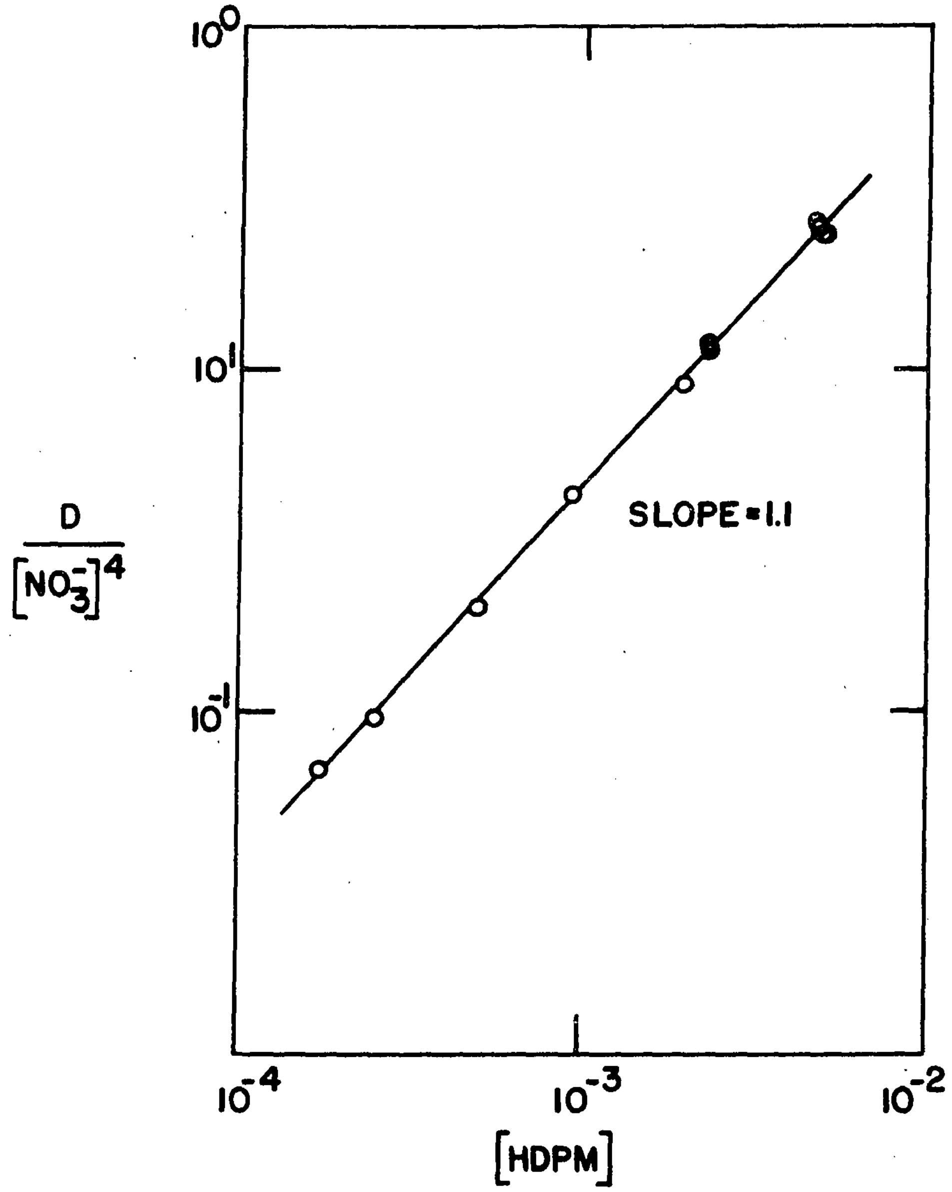


Figure 42. The extraction of $Th(NO_3)_4 \cdot HDPM$; solvent 1,2-dichlorobenzene (see Table 40)

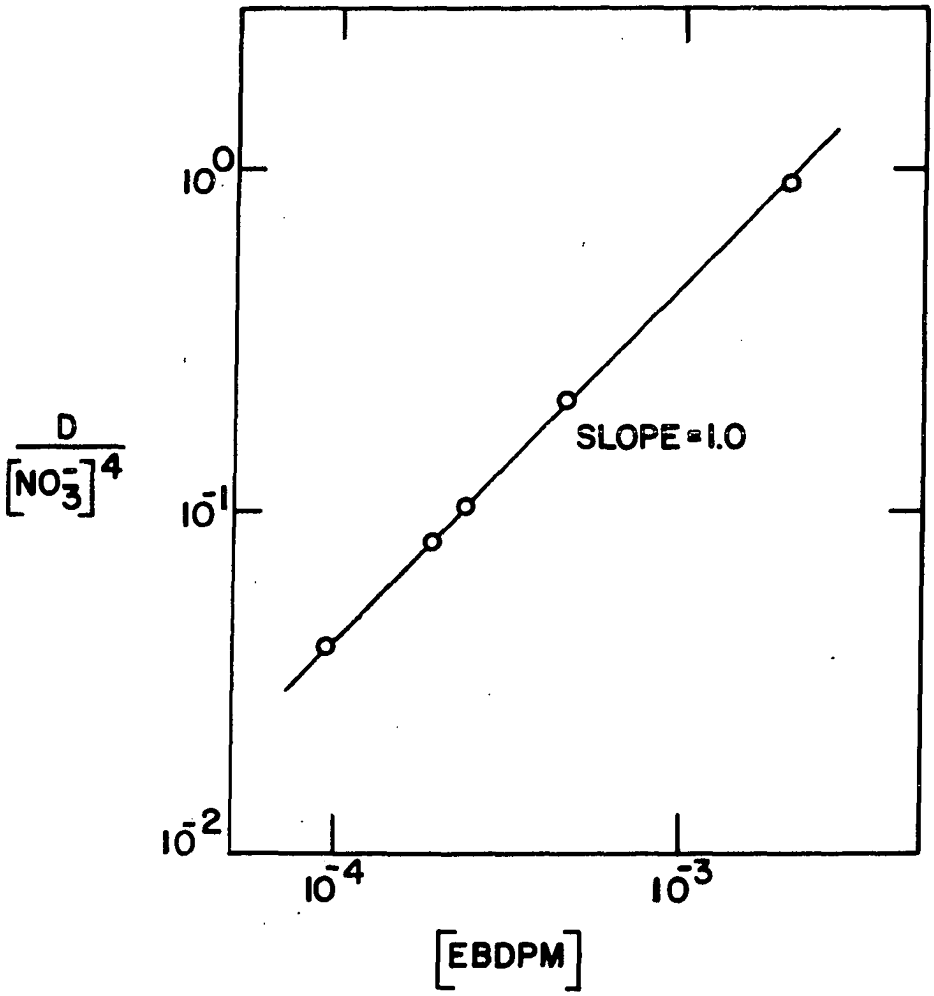


Figure 43. The extraction of $Th(NO_3)_4 \cdot EBDPM$; solvent = 1,2-dichlorobenzene (see Table 42)

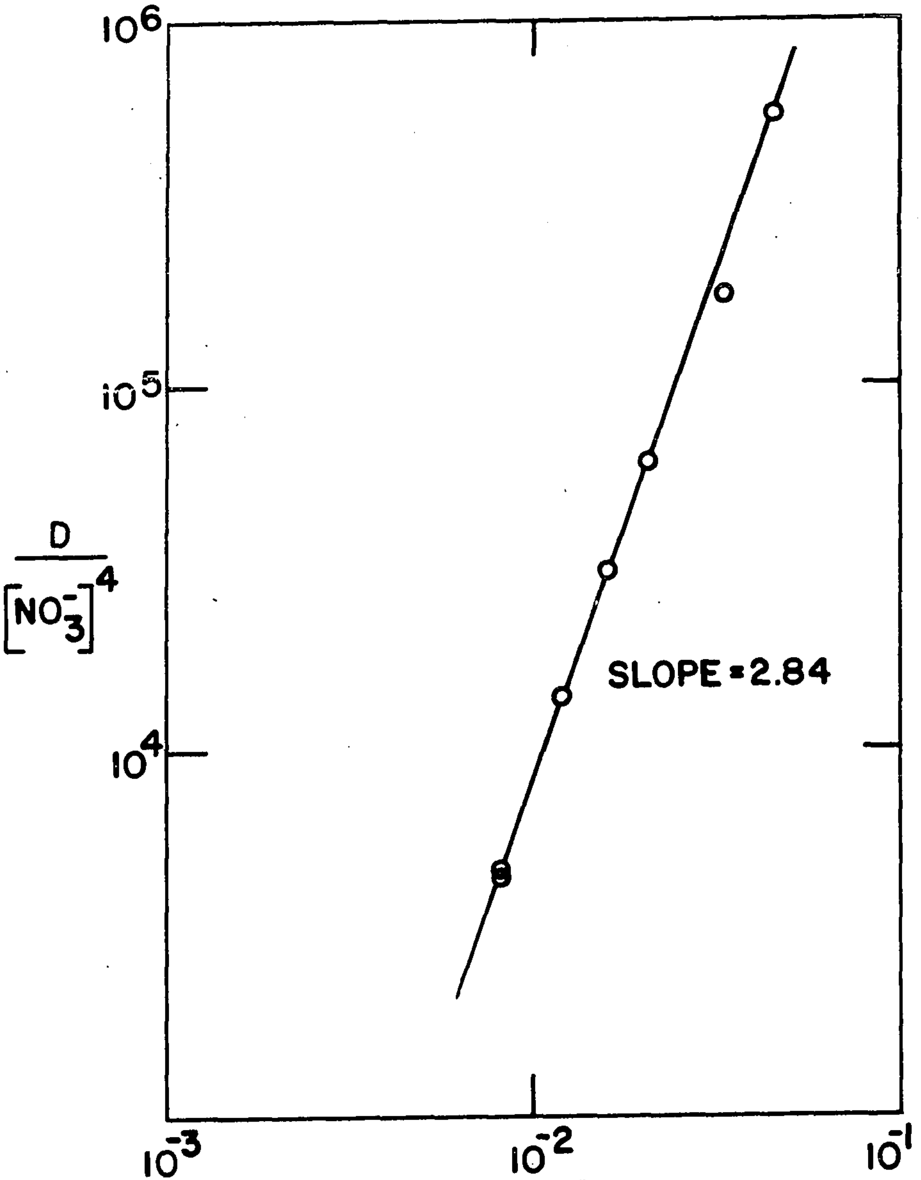


Figure 44. The extraction of $Th(NO_3)_4 \cdot 3TOPO$; solvent = 1,2-dichlorobenzene (see Table 43)

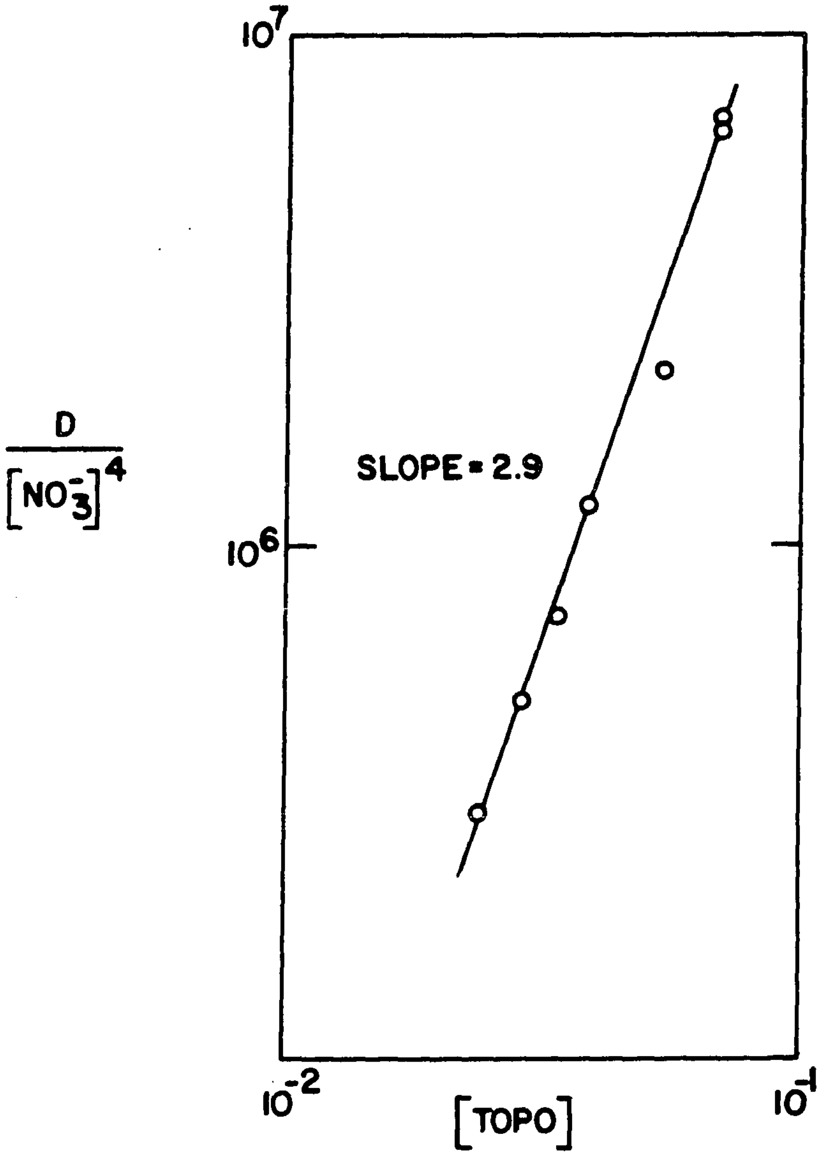


Figure 45. The extraction of $Th(NO_3)_4 \cdot 3TOPO$; solvent = cyclohexane (see Table 44)

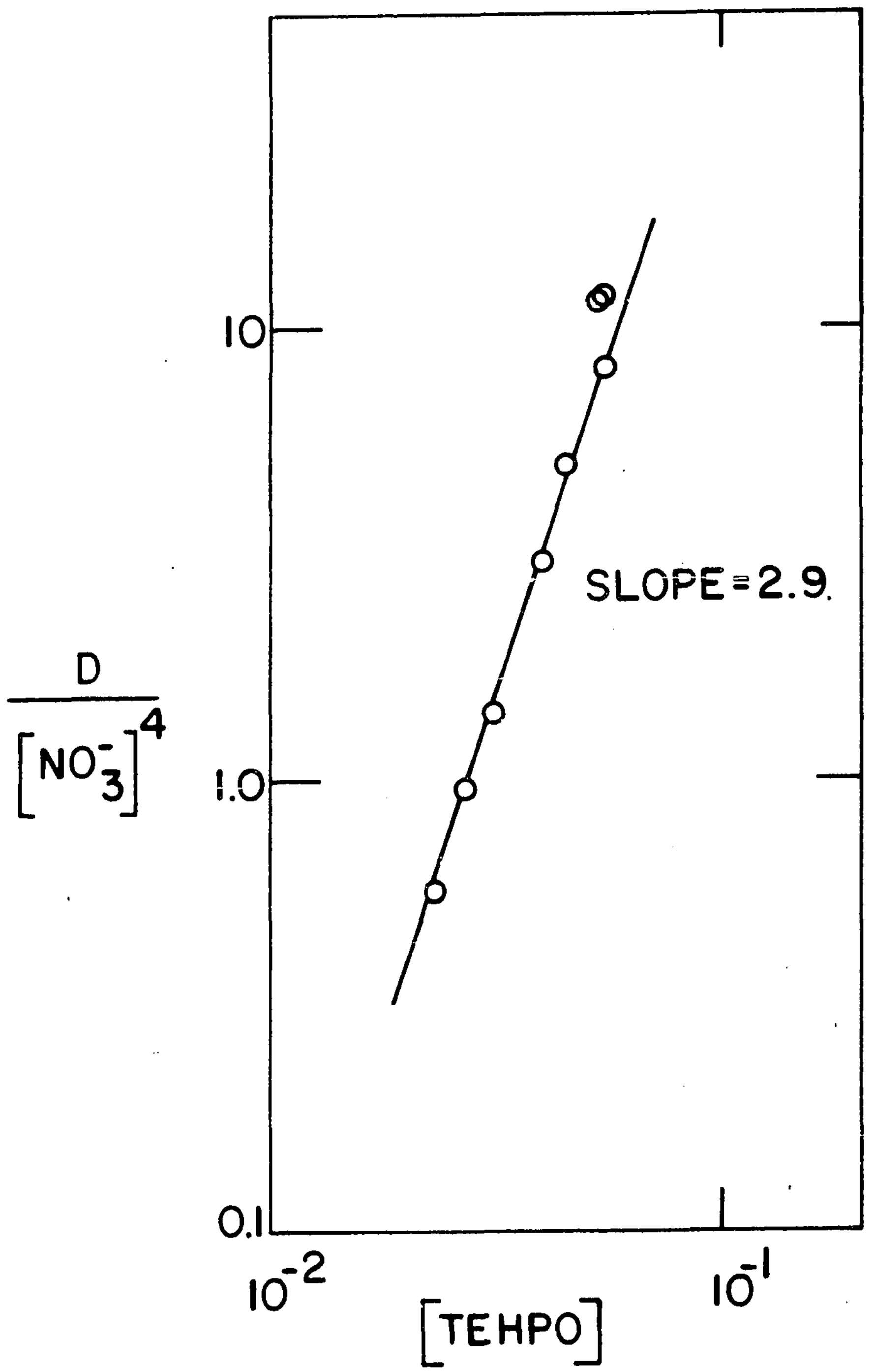


Figure 46. The extraction of $Th(NO_3)_4 \cdot 3TEHPO$; solvent = cyclohexane (see Table 46)

Conductivity Studies

The complexes of HDPM and TOPO with thorium nitrate were studied by determining the equivalent conductance (based on thorium nitrate concentration) as a function of ligand:metal ratio. Conductivity measurements were made by the use of an alternating current bridge. The circuit and equipment has been described by O'Laughlin (233). A cathode ray oscilloscope was used to indicate the balance point of the bridge. The conductivity cell was calibrated with solutions of potassium chloride and found to have a cell constant of 0.3463. A constant temperature bath maintained the temperature of all solutions at 25.0 ± .5°C. Spectral-grade acetonitrile was used as the solvent in preparing the solutions. Nitrobenzene was found to be unsuitable as a solvent because of the limited solubility of thorium nitrate in it. The equivalent conductance, Λ, of a solution of resistance R was calculated from the following expression where K is the cell constant and C is the thorium nitrate concentration.

$$\Lambda = \frac{1000\ K}{RC}$$

The results are shown in Figure 47.

The plot of equivalent conductance versus ligand:metal ratio for the $Th(NO_3)_4$-TOPO system shows a minimum in equivalent conductance at a 2:1 ligand:metal ratio. This is good evidence for the formation of a relatively unionized complex $Th(NO_3)_4 \cdot 2TOPO$. There is no distinct minimum in the plot of

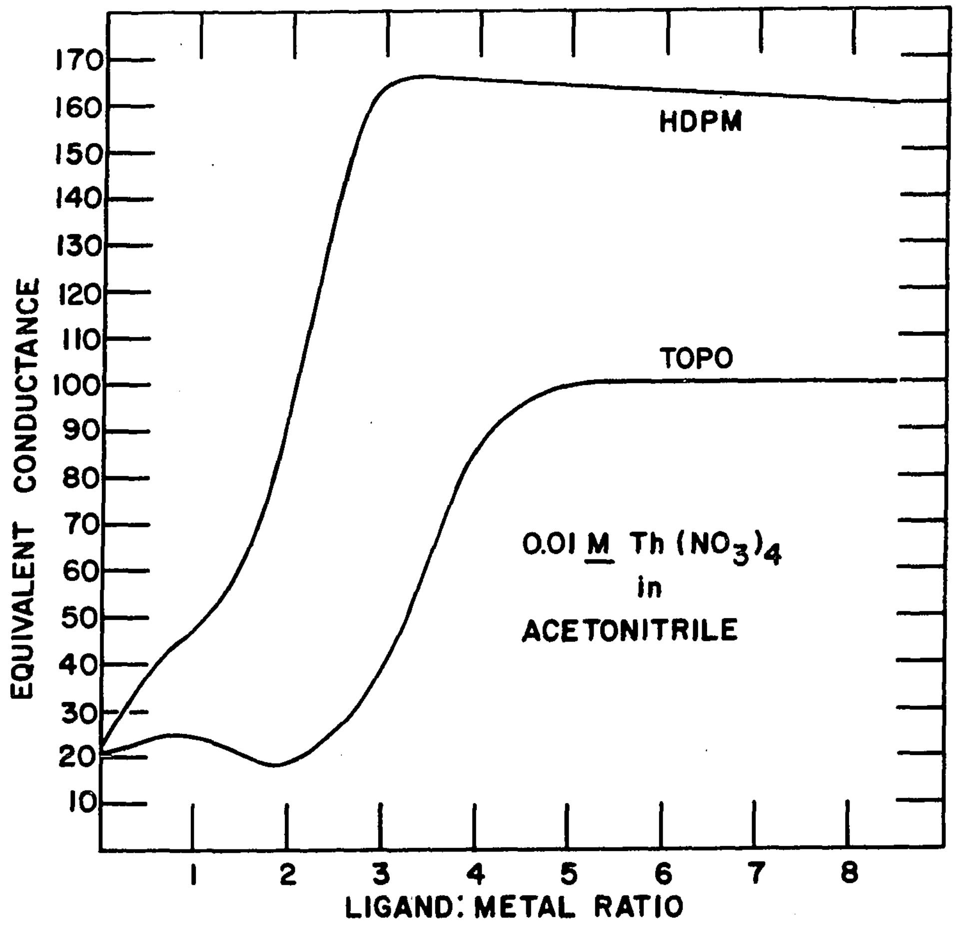


Figure 47. Effect of extractant on conductance of thorium nitrate

equivalent conductance versus ligand:metal ratio for the $Th(NO_3)_4$-HDPM system. There is, however, an inflection in the curve at a ligand:metal ratio of ~ 1:1. While this is evidence of complex formation, there is some doubt as to what structure should be assigned to it.

Preparation of Solid Complexes

Discussion

While studying the extraction of uranium(VI) nitrate and thorium nitrate, it was noticed that certain phosphine oxides gave precipitates when used as extractants. Those precipitates formed with bis(di-2-ethylbutylphosphinyl)-methane, EBDPM, and with bis(dicyclohexylphosphinyl)methane, CHDPM, were examined with the hope of obtaining some information on the nature of the extractable species.

The uranium(VI) complexes with EBDPM and CHDPM are yellow solids melting at 275°C (d.) and 300°C (d.), respectively. Elemental analyses show their compositions to be $UO_2(NO_3)_2\cdot$EBDPM and $UO_2(NO_3)_2\cdot$CHDPM. Molecular weight determinations confirm them to be monomers. Mrochek et al. (5) found a 1:1 complex to exist in solutions containing uranium(VI) nitrate and bis(di-n-hexylphosphinyl)methane. They calculated formation constants for both the 1:1 and 2:1 complexes. Healy and Kennedy (78) found that by saturating solutions of bis(di-n-butoxyphosphinyl)ethane, bis(di-n-butoxyphosphinyl)methane, or tetra-n-butyl pyrophosphate in benzene with $UO_2(NO_3)_2\cdot 6H_2O$

they could obtain 1:1 ligand:metal complexes. They regarded these complexes as being either chelates or polymers of the type $[UO_2(NO_3)_2 \cdot L]_n$ where L represents the coordinated organic ligand. Viscosity studies seemed to indicate that the polymeric structure was the correct one. Saisho (310) assumed the chelate structure, but the nature of his data does not seem to allow one to clearly distinguish between the two possibilities.

Healy and McKay (43) have reported that tri-n-butyl phosphate forms an anhydrous disolvate with uranium(VI) nitrate melting at -6.0°C and that tri-n-butylphosphine oxide forms a similar complex melting at 40°C. Burger (3) has prepared the following complexes: $UO_2(NO_3)_2 \cdot 2BuOP(O)Bu_2$, M.P., 56-7°C; $UO_2(NO_3)_2 \cdot 2(BuO)_2P(O)Ph$, M.P., 42-3°C; $UO_2(NO_3)_2 \cdot 2Bu_3PO$, M.P., 51-3°C; and $UO_2(NO_3)_2 \cdot 2Ph_3PO$, M.P., 289-293°C. There is some discrepancy in the two reported melting points for the 2:1 complex formed between tri-n-butylphosphine oxide and uranium(VI) nitrate.

The infrared absorption band of the phosphoryl group in the free EBDPM ligand occurs as a doublet with maxima at 1208 cm^{-1} and 1171 cm^{-1} (liquid film). Zingaro and Hedges (229) have observed a doublet for tris(2-ethylhexyl)phosphine oxide with maxima at 1198 cm^{-1} and 1164 cm^{-1} (CS_2 soln.). They have explained this doublet as arising from an equilibrium between one form of the molecule in which the 2-ethylhexyl groups are rotated so as to eliminate interaction among themselves and another form in which the 2-ethylhexyl groups are rotated so as to eliminate interaction between them and the phosphoryl group. This same explanation can apply to EBDPM. In addition there may be steric hindrance of rotation for the two halves of the molecule about the methylene bridge.

For the complex between EBDPM and uranium(VI) nitrate, a new band appears at 1148 cm^{-1} (film). As discussed by Cotton _et_ _al_. (283) the main effect observed when a metal is complexed with phosphoryl groups is a decrease in the amount of $p\pi \rightarrow d\pi$ back bonding in the $^{-}O \rightarrow P^{+}$ group which decreases the bond order and lowers the absorption frequency.

The infrared absorption band of the phosphoryl group in the free CHDPM ligand occurs at 1161 cm^{-1} (mull). Upon complexation with uranium(VI) nitrate, strong bands appear at 1129 cm^{-1} and 1136 cm^{-1} (mull).

The ultraviolet-visible absorption spectrum of a solution of the uranium(VI)-EBDPM complex dissolved in chloroform shows a broad band in the region 350-500 mμ with the principal maximum at 421 mμ and some fairly sharp fine structure showing maxima at 360, 369.5, 387, 397.5, 409, 433.5, 439, 453, 468.5, and 487.5 mμ. It is the type of spectrum that Kaplan _et_ _al_. (311) have classified as being caused by the neutral uranium(VI) dinitrate complex. The uranium(VI)-CHDPM complex is not soluble in a suitable solvent for either its ultraviolet-visible absorption spectrum or its nuclear magnetic resonance spectrum to be obtained.

O'Laughlin[1] has made conductivity studies using uranium(VI) nitrate and CHDPM in nitrobenzene. He found that a plot of molar conductance versus ligand:metal ratio showed a minimum in conductance at a 1:1 ratio. This is strong evidence that a 1:1 complex exists and that it is relatively unionized.

The nuclear magnetic resonance spectra of EBDPM and its uranium(VI) nitrate complex were obtained along with those of related compounds. When a phosphoryl compound such as tri-n-octylphosphine oxide, tris(2-ethylhexyl)phosphine oxide, or tri-n-butyl phosphate forms a complex with uranium(VI) nitrate, the resonance absorption of the protons on the α-carbon atoms is shifted downfield 0.5 to 0.6 ppm. Similar effects occur with compounds of the type, $R_2P(O)CH_2P(O)R_2$, for the protons on the α-carbon atoms in the R groups and even more strikingly so for the methylene bridge protons. In the spectrum of EBDPM, the methylene bridge protons appear as a triplet at 2.19 ppm in $DPCl_3$ (all chemical shifts referred to are downfield with respect to tetramethylsilane as an internal standard). While in the spectrum of the uranium(VI) complex, these protons appear as a triplet at 3.66 ppm. Another example of this large shift is that of bis(di-n-hexylphosphinyl)methane, HDPM, and its uranium(VI) complex. The methylene bridge protons for HDPM absorb at 2.05 ppm in CCl_4 while in the uranium(VI)-HDPM complex,

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[1] O'Laughlin, J. W., Ames Lab., Ames, Iowa. Conductivity studies. Private communication. 1963.

methylene bridge protons absorb at 3.62 ppm. In both cases the resonance absorption of the methylene bridge protons was shifted downfield approximately 1.5 ppm upon complexation with uranium(VI) nitrate and appeared as a triplet. Although uranium(VI) has no unpaired electrons, the uranyl ion is reported to have a small amount of paramagnetism (312). This is probably the reason for the large chemical shifts observed. Most important is the fact that in the spectra of the uranium complexes the methylene bridge protons appear as triplets. When the two phosphorus atoms are nonequivalent as in [di-n-heptylphosphinyl)(dihydroxyphosphinyl)]methane, then the methylene bridge protons appear as a quartet. The fact that the spectra show the methylene bridge protons as triplets in the uranium complexes is a good indication that the phosphorus atoms are equivalent and that the ligands are bidentate. Walmsley and Tyree (295) have prepared a number of transition metal complexes of bis(diisopropoxyphosphinyl)methane and bis(di-n-butylphosphinyl)methane in which the organic compounds apparently act as bidentate ligands.

Gatehouse et al. (296) and Bertin et al. (297) have devised criteria by which it is possible to distinguish between the nitrate ion and the nitrato group in metal nitrates. There is a decrease in symmetry in going from the nitrate ion to the nitrato group. This causes the NO_2 asymmetric stretching frequency (1380 cm^{-1} in KNO_3) to split into two bands occurring in the regions 1530-1480 cm^{-1} and 1290-1250 cm^{-1}.

In addition, the -O-NO_2 stretching frequency, theoretically inactive for nitrate ion, occurs as a strong band in nitrato complexes within the range 1034-970 cm^{-1}. Katzin (299) has added the restriction that the splitting of the NO_2 frequency must be of the order of 100 cm^{-1} or more before the nitrate can be considered to be coordinated. This restriction was necessitated by his finding a splitting of 65 cm^{-1} for the ionic nitrates in the lithium nitrate-tri-n-butyl phosphate complex. The smallest splitting observed for a compound definitely containing nitrato groups was 125 cm^{-1} for the calcium nitrate-tri-n-butyl phosphate complex. The uranium(VI)-EBDPM complex has absorption bands at 1516, 1300, 1280, and 1037 cm^{-1} (film) which can be attributed to nitrato groups. Similarly the uranium(VI)-CHDPM complex has covalent nitrate bands at 1512, 1490, 1291, and 1030 cm^{-1} (mull).

The coordination number of uranium(VI) is difficult or impossible to determine in complexes containing nitrato groups without resorting to x-ray analysis. One is always faced with the problem of whether a nitrato group is acting as a monodentate, bidentate, or tridentate ligand. Hoard and Stroupe (307) found by x-ray analysis that crystalline $Rb^+[UO_2(NO_3)_3]^-$ consists of a ring of six oxygen atoms in a plane at right angles to a central uranyl group. The nitrato groups were considered to be acting as bidentate ligands. Also using x-ray analysis, Fleming and Lynton (290, 291) found this same type structure to exist for the disolvated complex of uranium(VI) nitrate with triethyl phosphate. Because of the similarity between phosphate and phosphine oxide complexes and the proven existence of bidentate nitrato groups in some complexes, it is quite likely that the coordination number of uranium(VI) in $UO_2(NO_3)_2 \cdot EBDPM$ and in $UO_2(NO_3)_2 \cdot CHDPM$ is eight.

The complex between thorium nitrate and EBDPM melts at 263°C (d.) while that with CHDPM melts at 255°C (d.). Elemental analyses show their compositions to be $2Th(NO_3)_3 \cdot 3EBDPM$ and $Th(NO_3)_4 \cdot CHDPM$.

No solid thorium-phosphine oxide complexes are reported in the literature. Thorium nitrate has been reported to form a disolvate (43, 58, 67), a trisolvate (67, 133, 141), and a tetrasolvate (313) with tri-n-butyl phosphate and a trisolvate (205) with tri-n-octylphosphine oxide.

As with the uranium complexes, the infrared spectra indicate that in the thorium complexes the nitrates are coordinated and that the phosphoryl absorptions are shifted to lower wave numbers. In the thorium-EBDPM complex the nitrato groups absorb at 1521, 1281, 1266, and 1023 cm^{-1} with a strong band for the complexed phosphoryl appearing at 1104 cm^{-1} (film). The thorium-CHDPM complex has covalent nitrate bands at 1523, 1312, 1277, and 1027 cm^{-1} with two strong bands for complexed phosphoryl absorbing at 1126 and 1106 cm^{-1} (mull).

Experimental

The solid complexes with EBDPM were formed by shaking a solution of EBDPM in n-hexane with a solution of the metal nitrate in 1 M nitric acid. The precipitate which was formed was filtered off and washed with n-hexane. The CHDPM complexes were prepared by mixing alcoholic solutions of the ligand and the metal nitrate. The solid complexes were then filtered and washed with alcohol. The EBDPM complexes can also be prepared in this manner.

$UO_2(NO_3)_2 \cdot EBDPM$: Calculated: C, 35.63; H, 6.46; U, 28.25; molecular weight, 843. Found: C, 35.50; H, 6.40; U, 28.4; molecular weight 825.

$2TH(NO_3)_4 \cdot 3EBDPM$: Calculated: C, 39.06, H, 7.08, Th, 20.13; molecular weight, 2306. Found: C, 38.4, H, 6.70; Th, 20.2; molecular weight, 2424.

$UO_2(NO_3)_2 \cdot CHDPM$: Calculated: C, 35.97; H, 5.56; U, 28.52. Found: C, 35.5; H, 5.55; U, 28.2.

$Th(NO_3)_4 \cdot CHDPM$: Calculated: C, 32.61; H, 5.04; Th, 25.20. Found: C, 32.7; H, 5.19; Th, 24.0.

Molecular weights were determined cryoscopically in nitrobenzene. The complexes are insoluble in exaltone and cyclohexanol. Ultraviolet and visible spectra were obtained with the Cary Model 14 recording spectrophotometer. The infrared spectra of EBDPM and its complexes were obtained as film spectra on Eastman Kodak Irtran-2 optical material while those of CHDPM and its complexes were run as mulls in nujol and perfluorolube with sodium chloride cells. A Beckman-IR 7 infrared recording spectrophotometer was used. Proton spectra were run on a Varian Associates HR-60 high resolution nuclear magnetic resonance spectrometer.

SUMMARY

An extensive review of some of the more important neutral organophosphorus compounds as solvent extractants was given. The compounds included were tri-n-butyl phosphate, TBP, tri-n-octylphosphine oxide, TOPO, tris(2-ethylhexyl)phosphine oxide, TEHPO, and bis(di-n-hexylphosphinyl)methane, HDPM. A review was also given on the effects of structure on the extracting power of neutral organophosphorus compounds.

It was found that many phosphoryl containing compounds could be titrated as bases. By studying the extraction of nitric acid, a relative order of basicity was established for certain of the phosphine oxides. TOPO was found to be more basic than TEHPO, and HDPM was found to be more basic than bis(di-2-ethylbutylphosphinyl)methane, EBDPM, which in turn was more basic than bis(di-2-ethylhexylphosphinyl)methane, EHDPM.

The extraction of uranium(VI) nitrate, thorium nitrate, and samarium nitrate by TOPO, TEHPO, HDPM, EBDPM, and EHDPM was studied as a function of nitric acid concentration. From an examination of the distribution coefficients obtained, a number of generalizations were made: (1) bis(dialkylphosphinyl)methanes are better extractants than trialkylphosphine oxides; (2) compounds with straight chain alkyl groups are better extractants than those with branched-chain alkyl groups for both the bis(dialkylphosphinyl)methanes and the trialkyl-

phosphine oxides; (3) trialkylphosphine oxides and the more sterically hindered bis(dialkylphosphinyl)methanes are better extractants for uranium(VI) nitrate than for thorium nitrate; and (4) nonsterically hindered bis(dialkylphosphinyl)methanes are better extractants for thorium nitrate than for uranium(VI) nitrate. Uranium(VI) nitrate and thorium nitrate can be quantitatively extracted by any of the reagents while samarium nitrate is extracted to a much lesser extent.

Because highly basic phosphoryl groups are of little value in coordinating a metal atom if the groups are sterically hindered, it was of interest to see if any of the extractants being used showed evidence of having rotational isomers. The infrared spectra of the extractants were obtained. The phosphoryl band was a doublet in at least some of the spectra. It was found that the relative intensities of the two bands of the phosphoryl doublet were temperature dependent. This gave evidence for the existence of rotational isomers for EBDPM, EHDPM, and TEHPO. However, no confirming evidence could be found in their proton magnetic resonance spectra.

The structures of the complexes formed between thorium nitrate and TOPO, TEHPO, HDPM, and EBDPM were determined using saturation, equilibrium, infrared, and conductivity studies. The complexes found to exist in solution were $Th(NO_3)_4 \cdot 2TOPO$, $Th(NO_3)_4 \cdot 3TOPO$, $Th(NO_3)_4 \cdot 2TEHPO$, $Th(NO_3)_4 \cdot 3TEHPO$, $Th(NO_3)_4 \cdot HDPM$, $Th(NO_3)_4 \cdot 2HDPM$, $Th(NO_3)_4 \cdot EBDPM$, and $Th(NO_3)_4 \cdot 2EBDPM$. The nitrates are covalent in most of these complexes. However, the nitrates in $Th(NO_3)_4 \cdot 2HDPM$ and $Th(NO_3)_4 \cdot 2EBDPM$ appear to be partially ionic. With each ligand, the complex of higher ligand:metal ratio was the more stable one.

Crystalline complexes of uranium(VI) nitrate and of thorium nitrate were prepared with EBDPM and with bis(dicyclohexylphosphinyl)methane, CHDPM. These complexes were found to have the structures $UO_2(NO_3)_2 \cdot EBDPM$, $UO_2(NO_3)_2 \cdot CHDPM$, $2Th(NO_3)_4 \cdot 3EBDPM$, and $Th(NO_3)_4 \cdot CHDPM$. The complexes are of high thermal stability. The nitrates in all of these crystalline complexes are covalent. The proton magnetic resonance spectra of $UO_2(NO_3)_2 \cdot EBDPM$ indicates that, at least in this case, the ligand, EBDPM, is bidentate.

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