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Gas chromatography of mixed-ligand complexes of the lanthanides and related elements

Robert Frederick Sieck
Iowa State University

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OF THE LANTHANIDES AND RELATED ELEMENTS.

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Gas chromatography of mixed-ligand complexes of the
lanthanides and related elements

by

Robert Frederick Sieck

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Ames, Iowa

1971

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I. LITERATURE REVIEW AND THEORY

A. Introduction

This thesis will report an investigation of the basic facets of the determination of mixed-ligand complexes by gas chromatography. Chemical systems which form mixed-ligand complexes suitable for determination by gas chromatography, gas chromatographic columns suitable for the determination of mixed-ligand complexes and the performance of gas chromatographic detectors in the determination of mixed-ligand complexes have been studied. The review of the literature and presentation of theory will cover only those areas pertinent to these topics.

Due to the similarity in the determination of metal chelates and the determination of mixed-ligand complexes by gas chromatography (G.C.), the review of the literature will present a general survey of chemical systems used for determination of inorganic species by G.C. Included in this section will be a brief discussion of the literature and theory of solvent extraction as it applies to mixed-ligand complexes evaluated in this study.

The review of the literature and presentation of theoretical considerations concerning gas chromatographic columns

and detectors will be limited to material related to the determination of metal chelates and mixed-ligand complexes by G.C. The literature on electron capture detectors will not be extensively evaluated because this detector was not used in this work.

B. Chemical Systems Used for Determination of Inorganic Species by Gas Chromatography

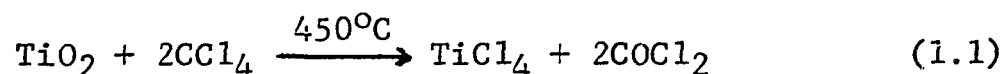
The determination of cations or metals by G.C. is a new technique which has developed rapidly in recent years. The gas chromatograph is not conveniently operated at temperatures in excess of 300°C. Hence, a compound to be determined by G.C. must be volatile at this operating temperature. This operating requirement puts a severe limitation on the types of inorganic compounds that can be chromatographed.

The types of metal compounds that are volatile at reasonably low temperatures are very limited in number. They include metal alkyls, metal alkoxides, metal carbonyls, metal hydrides, metal halides, π -bonded metal complexes such as the metal cyclopentadienyls, and β -diketonates (83,135). In order to be of use for practical analytical methods however, the metal compounds must not only be volatile, but must be formed in quantitative yield. A final requirement is that the metal

compound have sufficient thermal stability when volatilized so that it will not decompose during analysis by G.C. There are only two types of metal compounds which appear to meet all these requirements, the metal halides and metal- β -diketonates.

1. Metal halides

Pommier (92) has reviewed the determination of inorganic halides by G.C. up to 1966. A typical reaction for the formation of a volatile metal chloride is shown in Equation 1.1.



Sievers, Wheeler, and Ross (128) reported one of the first quantitative methods for determination of a metal by G.C. utilizing the reaction shown in Equation 1.1. Sievers et al. were able to quantitatively determine titanium in the range 0.02 to 0.17 mg of TiO_2 in bauxite samples. Several other workers have made contributions in the development of the determination of inorganic chlorides by G.C. (21,121,122). Table 1.1 shows the range of inorganic species which have been determined as chlorides.

Zvarova and Zvara (151) have recently reported the determination of the lanthanide chlorides by G.C. Al_2Cl_6 vapor was used as a component of the carrier gas, and Zvarova and Zvara suggested that compounds of the general formula LnAlCl_6 were

Table 1.1. Inorganic chlorides determined by G.C.

CCl_4	SCl_2	VOCl_3	AsCl_3
SiCl_4	SOCl_2	CrO_2Cl_2	SnCl_4
PCl_3	TiCl_4	Ga_2Cl_6	SbCl_3
POCl_3	VCl_4	GeCl_4	SbCl_5

being chromatographed, where Ln = lanthanide(III) ion.

Numerous inorganic species have also been determined by G.C. as fluorides. Juvet and Fisher (58) developed a method for synthesis and determination by G.C. of twelve different inorganic fluorides. Several other workers have been involved in solving some of the problems associated with determination of the highly reactive inorganic fluorides (30,31,48,118,137). Table 1.2 shows some of the inorganic fluorides which have been determined by G.C.

Table 1.2. Inorganic fluorides determined by G.C.

ClF	BF_3	MoOF_4	VF_5
ClF_3	SF_6	ReOF_5	VOF_3
ClO_2F	SeF_6	OsF_6	UF_6
SiF_4	TeF_6	WF_6	UO_2F_2

Although techniques for the analysis of inorganic species by G.C. of the chlorides and fluorides have been developed, these methods have not been widely applied. The inorganic halides are very reactive and thus pose special problems for synthesis, handling and analysis by G.C. (48,58).

2. Solvent extraction and gas chromatography of metal complexes

In recent years there has been a widespread interest in the determination of β -diketonates by G.C. Moshier and Sievers (83) published a very complete monograph on the gas chromatography of metal chelates which reviews the work done prior to 1965. Sievers and his co-workers have been principal contributors in this area of research (28,29,95,99,100,101,102,123,124,125,126,127,128,129,130).

In 1963 Sievers et al. (127) reported the gas chromatography of several metal chelates with H(ACAC), H(HFA) and H(TFA).¹ This paper reported the remarkable increase in volatility observed for chelates of fluorinated β -diketones as compared to those of acetylacetone. Sievers proposed that the increase in volatility may be due to a reduction in van der Waals' forces and possibly to a decrease in intermolecular

¹See APPENDIX for structures and nomenclature of ligands.

hydrogen bonding. The electronegative fluorine atoms would occupy a large portion of the outer periphery of octahedral complexes with ligands such as H(HFA) and hence the intermolecular attractive forces may be weaker than in analogous unfluorinated complexes.

A major portion of the work on determination of metal chelates by G.C. has utilized the ligand H(TFA). This may be due in part to the fact that chelates of H(TFA) are extracted better than some of the other fluorinated β -diketones (14). Table 1.3 lists metals which have been determined by G.C. as the H(TFA) chelates. The resolution of isomers of H(TFA) chelates has also been reported (26,127).

Table 1.3 Metals determined by G.C. as the H(TFA) chelates

Be	Zr ^a	Fe(III)	Pd ^a	In
Mg	Hf ^a	Fe(II) ^a	Cu	Th ^a
Ca ^a	Cr(III)	Co ^a	Zn ^a	
Al	Mn(III)	Rh	Cd ^a	
Sc	Mn(II) ^a	Ni ^a	Ga	

References: (1,41,51,69,80,81,82,99,100,101,102,104,
106,109,127,129,136)

^aDecomposition during determination by G.C. reported.

Several workers have employed thermal techniques such as thermogravimetric analysis, (TGA), to study the stability and volatility of metal chelates with H(TFA) (11,28,29). Thermal analysis has proven to be a great aid in the study of metal complexes which may be able to be determined by G.C. Thermogravimetric analysis can be obtained quickly and, if decomposition does occur while obtaining TGA data, it does not impair the operation of the instrument as is the case for G.C.

Morie and Sweet have developed solvent extraction techniques using H(TFA) to extract Al, Ga and In (80); and Al and Fe (81) into benzene with subsequent determination of the TFA chelates by G.C. Solvent extraction adds a dimension of selectivity to this analytical procedure. It also allows quick preparation of the TFA chelates for determination by G.C. because samples can be taken directly from the organic phase after extraction. A solvent-extraction procedure was recently used by Savory et al. (104) for microdetermination of Cr in biological materials by G.C. and Scribner et al. (109) studied the solvent extraction of Cu, Fe, and Al with H(TFA). Scribner and Kotecki (108) studied the solvent extraction of the divalent metals Ni, Co, Cu, Zn, Cd, and Pd with H(TFA) and isobutylamine. They reported that some of these mixed-ligand

complexes of the divalent metals were determined by G.C., but this work was not confirmed. Belcher et al. (9) have determined fluorinated Pb(II) β -diketonates by G.C. and mass spectrometry.

Since the work of Sievers et al. (127) illustrating the high volatility of metal chelates with H(HFA), there has been considerable interest in this ligand. Hill and Gesser (51) did a quantitative study of the determination of the H(HFA) chelates of Al, Be, and Cr by G.C. Ross and Wheeler (103) determined Cr(HFA)₃ quantitatively by G.C. Sievers et al. (126) succeeded in partially resolving isomers of Cr(HFA)₃ by G.C. using a column packed with powdered dextro quartz. Several workers have studied HFA chelates using thermogravimetric analytical techniques (11,28,39).

Interest in metal chelates of acetylacetone, H(ACAC), has continued even though these species have been shown to be much less volatile than chelates formed with fluorinated β -diketonates (127). Karayannis and Corwin (59) reported the determination of several metal chelates of H(ACAC) by high pressure G.C. and Biermann and Gesser (13) determined the Be, Al, and Cr chelates with H(ACAC) by G.C. Yamakawa et al. (149) reported the determination of 17 different ACAC chelates by G.C. Metal chelates with H(ACAC) have also been studied by thermal

techniques (11,12,28,107).

The successful determination of metal chelates by G.C. as shown in Table 1.3 and as discussed in the preceding material has been with metals which have exhibited a primary coordination number of $2n$, where n is the charge on the metal ion. This is the case, for example, with the tris-chelates of Cr(III) with H(TFA) or H(HFA). A special problem arises for metals which exhibit a primary coordination number of $2n + m$ where n is the charge on the metal ion and m is 1 or more. Various studies of the coordination chemistry of the lanthanides have indicated this latter situation to be the case with $m = 1, 2, \text{ or } 3$ with different chemical systems. An excellent summary of these studies is given in a review article by Moeller (78) on the coordination chemistry of the lanthanides. Numerous workers have studied the structure of complexes of the lanthanides with β -diketones (6,17,33,67,68,70,76,79,113). Usually the tris- β -diketonates of the lanthanides are eight coordinate and have been reported to have square antiprism geometry as shown in Figure 1.1 (6,76,78). The tetrakis- β -diketonates studied by Lippard et al. (67,68) are reported to have dodecahedral geometry.

The complex shown in Figure 1.1 is an illustration of the

tris-complex of a lanthanide ion with H(HFA). As can be seen from the drawing in Figure 1.1, after the formation of the complex with H(HFA) the lanthanide ion, m, still has two coordination sites left unfilled as shown at points A and B on the drawing. When β -diketonates of the lanthanides are formed, these two unfilled coordination sites will most likely be occupied by the solvent in which the lanthanide ions reside, namely water. The fact that the β -diketonates of the lanthanides tend to be hydrated complexes has raised problems both in the attempt to determine these complexes by G.C. and in the solvent extraction of the complexes. These two problem areas will be discussed in some detail.

Mitchell (77) has shown that hydrated β -diketonates of the lanthanides decompose during thermogravimetric analysis. Apparently the water in the coordination sphere of these complexes helps initiate thermal degradation at high temperatures. This thermal instability due to hydration makes it impossible to determine the β -diketonates of the lanthanides by G.C. To overcome this problem, Eisentraut and Sievers (29) synthesized 2,2,6,6-tetramethyl-3,5-heptanedione, H(THD). It was reasoned that the bulky side chains on H(THD) would sterically interfere with the extra coordination sites of the lanthanides so

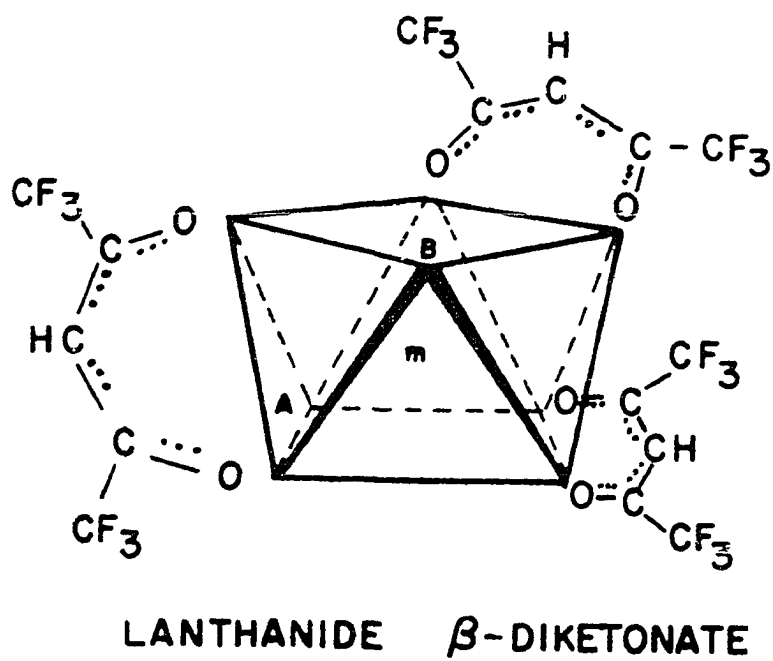


Figure 1.1. Illustration of a metal complex with square antiprismatic geometry

that anhydrous β -diketonates could be made. Eisentraut and Sievers (29) prepared solid anhydrous chelates of the lanthanides with H(THD) and reported the first successful determination of the lanthanides by G.C. Sicre et al. (119) did an extensive evaluation of the thermal characteristics of the chelates of the lanthanides with H(THD).

Springer, Meek, and Sievers (130) prepared the β -diketone 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, H(FOD). This ligand retained the desired steric effect of the β -diketone H(THD) and had the added advantage of increased volatility which was produced by the fluorine constituent.

Springer et al. isolated chelates of the lanthanides with H(FOD) as monohydrates which were easily dehydrated without decomposition under vacuum conditions. These anhydrous chelates were determined by G.C. and proved to be much more volatile than the chelates of H(THD). Since this work, other researchers have used fluorobutyl derivatives to increase volatility of various species (143).

Two independent Japanese research groups, Shigematsu et al. (114) and Tanaka et al. (134), synthesized 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione, H(PTA). This ligand, very similar to the one developed by Springer et al., was used to make anhydrous chelates of the lanthanides which were reported to

have been determined by G.C.

Lippard (67), Lippard, Cotton, and Legzdins (68), and Belcher et al. (7,8) have studied some volatile tetrakis-complexes of the lanthanides using mass spectrometry. Chelates of the composition $A(M)L_4$ were studied where A = alkali metal, M = lanthanide, and L = β -diketone.

None of the work discussed to this point allows the direct preparation of complexes of the lanthanides for determination by G.C. Sweet and Parlett (132) studied the extraction of the lanthanides with H(THD). This extraction was not quantitative for all the lanthanides, and it was not demonstrated that the extracted complexes could be determined by G.C. Sievers et al. (129) reported a technique for the direct preparation of $Fe(FOD)_3$ by heating finely powdered iron with H(FOD) in a sealed container, however, the technique was not shown to work with the lanthanides.

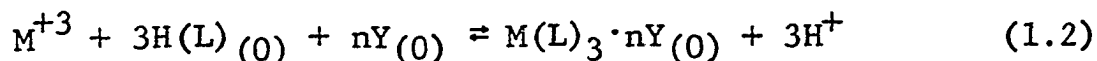
The difficulty encountered in the extraction of the lanthanide β -diketonates is also related to the fact that these β -diketonates are hydrated. Apparently the water in the coordination sphere makes the complex somewhat hydrophilic in nature so that it is not efficiently transferred to the organic phase in a solvent extraction. It has been found that an organic base such as tri-n-butylphosphate will displace the

water from the coordination sphere of a lanthanide β -diketonate (36). The resulting mixed-ligand complexes are hydrophobic and have been found to extract quantitatively. The nature of the extraction of mixed-ligand complexes of the lanthanides has been widely studied (14,16,27,36,91,110,111,115). The research on mixed-ligand extractions, commonly referred to as synergic extractions, has been thoroughly reviewed by Carey (16). Mitchell (77) has recently studied synergic extraction systems which employ fluorinated β -diketones in an effort to identify mixed-ligand complexes which are volatile and which are extracted quantitatively.

Carey (16, p. 103) has outlined a procedure for verification of the neutral donor content of the extracted complexes obtained in mixed-ligand extractions of the lanthanides. The procedure is based on the fact that the lanthanides are extracted very poorly by β -diketones in the absence of an organic base or neutral donor. Thus the concentration of $M(L)_3$, where M = lanthanide ion and L = β -diketone, in the organic phase of the solvent extraction mixture will be very small in comparison to the concentration of the mixed-ligand complex $M(L)_3 \cdot 2Y$, Y = neutral donor. Therefore the $M(L)_3$ species will contribute very little to the fluorescence or

absorbance of the organic phase in an extraction mixture.

The formation of a mixed-ligand complex in an extraction of the lanthanides is represented by the reaction shown in Equation 1.2.



The subscript, (0), specified the organic phase. When the initial concentration of β -diketone, H(L), is kept constant and in excess, and the concentration of H^+ is kept at a low level (pH = 5.5), the equilibrium is shifted to the right and the amount of neutral donor, Y, becomes the limiting factor in the extraction. One hundred per cent extraction of the lanthanide will occur, therefore, when the stoichiometric amount of neutral donor is added. The extraction of lanthanides such as Er and Nd can be followed by spectrophotometric analysis of the organic phase (133), while the extraction of Eu can be followed by measurement of the fluorescence of the organic phase (16). Thus, measurement of the extraction of a known amount of metal can be measured in relation to the amount of neutral donor present in the extraction. The comparison can be used to verify the amount of neutral donor present in the extracted mixed-ligand complex by determining the amount of neutral donor present when extraction is complete.

The application of mixed-ligand complexes to the extraction of the lanthanides with subsequent determination by G.C. was first reported by Butts and Banks (15). This technique allowed the direct preparation of anhydrous complexes of the lanthanides since the organic phase containing the extracted species could be sampled and injected into the chromatograph. The use of solvent extraction in combination with gas chromatography affords the possibility of exploiting the specificity of solvent extraction techniques in combination with the resolution capabilities of G.C. to achieve useful analytical methods.

Mixed-ligand complexes of UO_2^{+2} and Th(IV) have also been studied. $\text{UO}_2(\text{L})_2 \cdot \text{Y}$ and $\text{Th}(\text{L})_4 \cdot \text{Y}$ are reported as being formed in mixed ligand extractions of UO_2^{+2} and Th(IV) where L = β -diketone and Y = neutral donor (40,50,53,54,120,148). Shigematsu et al. (116) have used a β -diketonate of uranium in a coprecipitation method for uranium. On the other hand, several attempts have been made to analyze Th(IV) β -diketonates by G.C. (106,136,149). Yamakawa et al. (149) report a peak for thorium acetylacetonate, $\text{Th}(\text{ACAC})_4$. Tanikawa et al. (136) report a peak for $\text{Th}(\text{TFA})_4$ while Schwarberg et al. (106) were not able to obtain a chromatogram for $\text{Th}(\text{TFA})_4$.

Berg and Acosta (11) have reported volatile and stable acetylacetonates for Th(IV), U(IV), and UO_2^{+2} . They also

reported volatile chelates of thorium using H(HFA) to give Th(HFA)_4 and H(THD) to give Th(THD)_4 . Th(TFA)_4 was found to be volatile and stable by Berg and Acosta, but they found $\text{UO}_2(\text{TFA})_2$ to be thermally unstable. Swain and Karraker (131) studied U(IV) and Th(IV) chelates of H(THD) and H(FOD). They found U(THD)_4 , Th(THD)_4 , U(FOD)_4 , and Th(FOD)_4 chelates to be volatile, but observed no significant difference in volatility between the U(IV) and Th(IV) chelates. Mitchell (77) has reported the complex $\text{UO}_2(\text{HFA})_2 \cdot \text{TBP}$ to be volatile.

C. Gas Chromatographic Columns

The core of gas chromatography is the column in which separation of the sample components takes place. Since the overwhelming majority of gas chromatographic analyses have been done using liquid stationary phases (52), the gas-liquid chromatographic column is of particular interest. A gas-liquid chromatographic (GLC) column is a binary system in which a liquid phase is evenly loaded on a finely dispersed solid support which is packed into a column to provide a large interfacing surface area with the mobile phase or carrier gas which carries the sample components through the column. The uses of GLC columns may be divided into three general classes (150), a. analytical uses, b. preparative uses, and c. as a

media for the study of physico-chemical properties. Although GLC columns have been widely used for analysis, few workers have probed their potential for physical measurements. However, as Purnell (93) points out, studies of column performance can yield information about solubility, adsorption, thermodynamic quantities and diffusion.

The theory of partition chromatography has been thoroughly explicated by Giddings (43). However, some of the special theoretical aspects of GLC columns have not been well summarized and will therefore be discussed here. Waksmundzki (145) suggests that for GLC columns at least five phenomena may occur in the chromatographic system: a. partitioning of molecules of solute between the gas and the liquid phase, b. adsorption of solute molecules on the surface of the liquid phase, c. adsorption of solute molecules from the liquid solution by the support surface, d. adsorption of solute molecules from the gas phase by bare surface of the support (i.e., not covered by the liquid phase), e. change of composition and character of the liquid phase due to adsorption of its components. These five phenomena will be discussed with reference to research on various aspects of GLC columns.

1. Partitioning of molecules between the gas and the liquid phase

Distribution theory of solute distribution between two phases in equilibrium has been employed in the major separation techniques of extraction, distillation, countercurrent distribution, and various forms of chromatography (20). This theory was applied to GLC by James and Martin (56) and is the basic model used to develop an understanding of GLC column phenomena.

The retardation factor, R_f , is frequently used to describe the relative rate at which a solute band maximum moves through a column. For GLC columns:

$$R_f = t_M/t_R \quad (1.3)$$

where t_M = the time required for the carrier gas to pass through a column of length L , and t_R = the time for the solute band to travel the same distance. An equivalent ratio can be written (20,52),

$$R_f = V_M/V_R^{\circ} , \quad (1.4)$$

where V_M = the gas volume in the column, V_R° = the corrected retention volume of the solute adjusted for temperature, pressure differential and dead volume. However, a more commonly used expression in GLC column studies relates the corrected

retention volume, V_R^0 , to the partition coefficient, K ,

$$V_R^0 = V_M + KV_L \quad (1.5)$$

where V_L = the volume of the liquid phase in the column, and

$$K = \frac{\text{amount of solute per unit volume of stationary phase}}{\text{amount of solute per unit volume of mobile phase}}$$

Equation 1.4 assumes that the gas phase is incompressible, that there is equilibrium distribution of solute molecules between phases and that there is no adsorption of solute by the solid support or the liquid phase. Giddings (43) has pointed out that if retention is due to several simultaneous mechanisms it is possible to generalize Equation 1.5 as follows:

$$V_R^0 = V_M + \sum K_i V_{Li} \quad (1.6)$$

where K_i is the partition coefficient, and V_{Li} is the volume element of the i th phase. This general equation will be useful in the following discussion of various GLC column phenomena.

2. Adsorption of solute molecules on the surface of the liquid phase

When the liquid phase is spread out on a solid support as in GLC columns, the surface-to-volume ratio is very high so that any difference between the concentration of solute in the

bulk and in the surface can be significant to the equilibrium phenomena. Martin (72) observed that the elution order from GLC columns containing polar liquid phases changed as a function of the ratio of liquid phase to the solid support.

Martin proposed that adsorption at the liquid-gas interface caused the changes in solute elution order. A new equation for retention volume, V_R^C , was given to account for this adsorption. Assuming that the contribution to the retention volume from adsorption on the liquid surface is proportional to the surface area of the liquid, Equation 1.5 can be modified as follows:

$$V_R^O = V_M + KV_L + k_a A_L \quad (1.7)$$

where A_L = the surface area of the liquid per gram of packing and k_a = a proportionality constant. The equation can be further simplified by determining V_M for a material for which $K = 0$ (3). Hence

$$V_R^O = V_M = V_R^I = KV_L + k_a A_L \quad (1.8)$$

where V_R^I = the net retention volume. Martin found Equation 1.7 to describe the retention behavior of n-hexane on Chromosorb P and Chromosorb W columns containing varying percentages of β, β' -thiodipropionitrile. The nature of Chromosorb and other solid supports for GLC has been reported (63,88,105).

Martin (71) related Equation 1.8 to the Gibbs' Adsorption Equation and thereby provided the possibility for checking his hypothesis by study of independent systems. A common form of the Gibbs' Adsorption Equation (46) which describes solute concentrations at liquid-gas interfaces is:

$$\Gamma = - \frac{X}{RT} \frac{d\gamma}{dX} \quad (1.9)$$

where X = mole fraction of solute in the bulk liquid, $d\gamma/dX$ = the rate of change of the liquid surface tension with solute concentration and Γ = the excess of solute at the surface, in moles/cm², over that in an imaginary system in which the liquid retains the bulk composition up to an infinitely sharp interface. Dimensional analysis shows k_a in Equation 1.7 to have the dimensions of unit length. The quantity k_a is equal to the moles of solute per unit area of surface in excess to that in the bulk stationary phase divided by the moles of solute per unit volume of the gas phase. Thus, combining the definitions for k_a and for K , it is found that k_a/K is equal to the moles of solute per unit area of surface in excess to that in the bulk stationary phase divided by the moles of solute per unit volume of the bulk liquid. It can be seen that k_a in this expression is identical to Γ in Equation 1.9. Since K can be expressed as X times n_L , where n_L = the moles

of liquid phase per unit volume of liquid phase, and X is defined as in Equation 1.9, the following can be written:

$$\Gamma = \frac{k_a}{K} X_{nL} = - \frac{X}{RT} \frac{d\gamma}{dX} . \quad (1.10)$$

With Equation 1.10, adsorption measured by GLC can be compared directly with results obtained from static measurements utilizing the Gibbs' Equation.

It has been argued (75) that this model is not correct. Guggenheim (47) has stressed that the Gibbs' Adsorption Equation is derived for plane interfaces and may safely be applied to curved interfaces only provided that the thickness of the surface layer is small compared with its radius of curvature. In GLC columns, the liquid layer is of varying thickness and is spread throughout narrow pores of various contours and diameters so that it is unlikely that this condition is met. In addition, different workers (40,139) have reported effects attributed to the solid support up to 10-20% liquid coatings and it is therefore suggested that the observations of retention effects attributed to solute adsorption at the gas-liquid interface could be explained by resort to other models.

The extensive study of Pecsok (90) however, has verified Martin's original observations. Martire (73,74) and Pecsok (89) carried out static measurements of activity coefficients

and surface tensions at very low mole fraction which corroborated Martin's GLC data and hence substantiated his hypothesis of adsorption at the gas-liquid interface in GLC columns.

Martire (74) has identified two distinct classes of adsorption at the gas-liquid interface. The first class, which apparently produces the largest surface effects, occurs when the solute activity is large. In this case the less polar the solute is with respect to the solvent and the less soluble it is in the bulk liquid, the larger the solute surface excess concentration. The second class is characterized by low solute activity, significant solute solubility in the bulk liquid, and a solute and solvent molecule of comparable high polarity. Pecsok (89) found that liquid surface adsorption of the solute can also be an important feature of polar solute-nonpolar solvent systems in GLC columns.

3. Adsorption of solute molecules from the liquid solution by the support surface

For this phenomenon to occur, the solute molecules must diffuse through the liquid phase on the GLC column. This diffusion in the liquid phase would certainly be the rate determining step in such solute interaction, however rough calculations by Keller (61) indicate that under the conditions normally employed in gas chromatography, the solute would

have time to reach the support and be absorbed. Giddings (43) derives equations expressing theoretical plate height for GLC columns in which adsorption of solute molecules from the liquid solution by the support surface occurs. However this phenomenon, although possible, has not yet been confirmed by experimental evidence for GLC columns. Keller (61) suggests that if such a column interaction of the solute is occurring that it is not seen because the effect on retention is very small compared to the effect of other interactions.

4. Adsorption of solute molecules from the gas phase by bare surface of the support

Sorption studies have been carried out with GLC columns using varying amounts of liquid phase. Urone (139,140) obtained absorption isotherms for acetone on squalane coated surface active supports, that is supports which have not been treated to deactivate silanol and other adsorption sites. This system was found to follow a Freundlich isotherm equation up to 1 to 2% loading,

$$a = k_x P^{1/n} \quad (1.11)$$

where a = the amount of solute adsorbed per gram adsorbent,
 P = the pressure of the solute, and k_x and n are constants.
Waksmundzki (146) in a study of the effect of the amount of

binary fixed liquid phases on retention behavior and adsorption properties of GLC supports found adsorption behavior similar to that observed by Urone.

Keller (61,62) has proposed an equation to express the retention time of a solute in a GLC column in which the solute is in near equilibrium distribution with three phases. This equation is an extension of the generalized expression (Equation 1.6) discussed above.

$$V_R' = KC_L + k_S A_S \quad (1.12)$$

where V_R' , K , and V_L are as defined previously, A_S = area of the bare support surface, k_S = the ratio of the concentration of solute adsorbed by the solid support to the solute in the gas phase. It is clear that at high levels of liquid loading, that is 2% and above, the area of bare support, A_S , will go to zero and this retention expression reduces to Equation 1.5, the standard retention expression for gas-liquid partition chromatography.

5. Change of composition and character of the liquid phase due to adsorption of its components

It was noted in the discussion of solute adsorption on the surface of the liquid phase that some workers (40,139) have attributed unusual retention effects to solid support interaction with the solute even with liquid loadings as high

as 20%. Craig (18) argues against the concept of solid support interaction at such high liquid loadings because the surface of a GLC support appears to be completely covered at around 0.5 to 2% liquid loading. Craig suggests the possibility of orientation of the liquid phase molecules due to liquid-solid interaction and a consequent modification of the structure of the liquid phase.

The experimental work of Urone (139, 141) and Waksmundzki (146) offers evidence to confirm Craig's hypothesis. In studying the support effects on retention volumes for the retention of acetone on squalane coated columns, Urone (139) found that the retention volumes undergo a minimum at low percentage liquid phase loadings (about 0.6%) and a maximum at about 2% liquid phase loading. He suggested that the minimum in retention volume occurring at about 0.6% liquid phase loading could represent the effect of a mono-molecular layer of squalane, while the increase of retention volume to a maximum at about 2% liquid phase loading could represent the effect of a strongly oriented second layer. In further sorption studies, Urone (141) attributed an identifiable minimum adsorption in the adsorption isotherms at about 0.6% liquid loading to the adsorption by a monolayer of the liquid phase being used on the column.

In light of the work of Urone and Waksmundzki, it would appear that a correction should be made to Keller's suggestion (61) that at low liquid levels, where there is complete liquid coverage of the support, constant support effects are still manifest. The evidence points rather to the existence of retention effects arising from solute interaction with monolayers or highly oriented secondary layers of the liquid phase on the solid support.

This phenomena could be accounted for in a general retention equation as follows,

$$V_R' = k_o V_o \quad (1.13)$$

where k_o = the ratio of the concentration of solute in the oriented liquid phase to the concentration of solute in the gas phase and V_o = the volume of oriented liquid phase.

A general equation for the retention of a solute on a GLC column can be written by combining the various factors which have been discussed. Such an equation would relate all the possible factors contributing to retention of a solute in a GLC column as follows,

$$V_R' = KV_L + k_a A_L + k_s A_s + k_o V_o \quad (1.14)$$

where KV_L represents the contribution to retention from partitioning of the solute between the gas and the liquid phase,

$k_a A_L$ represents the contribution to retention from adsorption of the solute on the surface of the liquid phase, $k_s A_S$ represents the contribution to retention from adsorption of the solute on the bare support, and $k_o V_o$ represents the contribution to retention from a monolayer or a few highly oriented layers of the liquid phase which have been modified by adsorption on the solid support.

Which specific terms in Equation 1.14 will predominate in determining the retention of a solute will, of course, depend on the particular experimental situation. As has been seen in the experimental work reported above, different terms predominate depending on whether the solid support material has been deactivated or not, and depending on the relative polarities of the liquid phase and the solute. However, it is clear that in any case it is far too great a simplification to assume that only partitioning of molecules between the gas and the liquid phase is occurring in a GLC column.

In work with GLC columns, corrections for surface chemical phenomena must be made in order to apply gas chromatographic techniques to the determination of partition coefficients, activity coefficients, and other thermodynamic properties. Young (150) cites evidence that this precaution has not been sufficiently observed in research using GLC columns for the

determination of physicochemical properties. The particular type of interaction which is involved for a given system can be ascertained with a few simple experiments.

Except under special experimental conditions, it can be assumed that the contribution to retention of a solute from a monolayer or a few highly oriented layers of the liquid phase, k_0V_0 , is negligible (139,141,146). The general retention Equation 1.14 then reduces to the following,

$$V_R' = \frac{C_L}{C_g}V_L + \frac{L}{C_g}V_L + \frac{S}{C_g}A_s \quad (1.15)$$

where the constants K , k_a , and k_s have been replaced by the appropriate concentration terms: C_L = concentration of solute in the liquid phase, C_g = concentration of solute in the gas or mobile phase, L = surface excess for the liquid, S = surface adsorption by the solid support. From Equation 1.15 it can be seen that when C_g is sufficiently small, $L/C_g = k_a$ and $S/C_g = k_s$, Equation 1.14 will be accurate, and V_R' will not be a function of the concentration of solute. However, for both L and S there will be values of C_g sufficiently large so that L and S approach monolayer values and become constant. In this range V_R' will not be a constant, but will plot linearly against C_g^{-1} .

A final question is whether C_L/C_g is a constant or equal to zero. If C_L/C_g is a constant, V_R' should not be a function of the concentration of solute. If V_R' is a function of concentration other than that mentioned above, column overloading, dimerization, or other non-equilibrium conditions are indicated. The ratio C_L/C_g or K can be determined to be non-zero by studying V_R' as a function of different liquid loadings for GLC columns. If V_R' varies linearly with loading for the liquid phase of the GLC column, partitioning is indicated, that is $K \neq 0$.

Veening and Huber (142) have studied the partitioning of metal chelates on GLC columns and found the retention, V_R' , to be a function of partitioning of the metal chelates with the liquid phase, KV_L , and a function of adsorption by the solid support, k_sA_s . Gere and Moshier (42) calculated some thermodynamic values for the GLC determination of $Yb(THD)_3$. Details for such calculations have been reported (20,46,52). Uden and Jenkins (138) reported some unusual adsorption and displacement effects in the determination of metal β -diketonates by G.C.

The nature of various liquid phases used in G.C. has been reported (20,32). Most workers have used silicones or fluoro-silicone liquid phases in gas chromatographic columns used for

the determination of metal chelates (41,42,51,69,80,81,99,100, 101,102,103,104,106,127,129,130,134,136,149). The hydrocarbon type liquid phases such as Apiezon greases were not found to be very satisfactory (29,42,142).

The use of lightly loaded GLC columns has been discussed by Frederick et al. (38). Most of the early work done on determination of metal complexes by G.C. utilized lightly loaded columns (83). However, more recent studies, including most of those discussed above, have used 2 to 10% liquid loadings to achieve better partitioning and better resolution.

D. Gas Chromatographic Detectors

The most commonly used detectors in gas chromatography are the thermal conductivity, TC, detector and the flame ionization detector, FID. Details on the construction and operation of these detectors are available in general works on G.C. (20,32). Since these detectors have been widely available for use, it is not surprising to find that the FID and the TC detector have been most used for analysis of metal chelates.

The TC detector has been the most common choice for detection of metal chelates (20,80,81,82,106,123,124,129,130, 135,136,149). The TC detector has proven to be rugged and stable with moderate sensitivity. The minimum detection

limits for TC detectors are about 2 to 5 micrograms (20).

The FID has also been used for determination of metal complexes (13,15,51,127,142). The FID is more sensitive than the TC detector with minimum detectable quantities being about 10^{-10} gram (20).

Several workers have studied the response of the TC detection and the FID to various species (1,22,37). It has been reported that the FID response varies as a function of the metal in the determination of metal complexes by G.C. (14,51).

Recently there has been great interest in specific detectors for G.C. The use of alkali halides in the flame of the FID to form the so-called alkali flame ionization detectors, AFID, has been widely studied (5,23,24,25,44,45,55,57,60,147). The AFID has shown enhanced response, specifically for compounds containing P, N, As, S, and Cl. Janák et al. (57) suggest that the enhanced response for P, N, and As has to do with the interaction of solid acidic oxides formed from these species in the flame with alkali metal ions. Janák argues that a different and as yet unknown mechanism is involved for Cl. No connection has been made between this type of response behavior and the unusual FID response noted for metal complexes (14,51).

Ross and co-workers (98,99,100,101,102,103) have studied the application of the electron capture (EC) detector to the determination of metal complexes. The design and operation of the EC detector are discussed by Ettre and Zlatkis (32). The EC detector has a minimum detection limit of 10^{-12} to 10^{-13} gram for compounds containing halogens. Hence, metal complexes using fluorinated β -diketones can be detected at the ultra trace level. Several workers in addition to Ross have developed techniques for metal complexes utilizing the EC detector (1,41,86,104).

II. PURPOSE

The widespread application of gas chromatography for determination of inorganic species has been reported in the first section of this thesis. The analytical power of this application could be enhanced by development of techniques which employ both the procedures of solvent extraction and gas chromatography. The specificity offered by solvent extraction in combination with the resolution offered by gas chromatography afford the possibility of opening up new practical analytical techniques for cationic mixtures.

The feasibility of such a combination of procedures has been shown by Butts (14) who reported the solvent extraction and subsequent determination by gas chromatography of the H(HFA)-TBP mixed-ligand complexes of the lanthanides. Mitchell (77) has recently made an extensive investigation of the solvent extraction of mixed-ligand complexes which may be of use in determination of metals by gas chromatography. A review of the work by Butts reveals the following points:

1. The mixed-ligand complexes of the lighter lanthanides - La, Ce, Pr, and Nd - were reported to partially decompose under normal gas chromatographic conditions. Skewed chromatographic peaks were obtained for the

mixed-ligand complexes of these lanthanides.

2. The retention times for the mixed-ligand complexes of the lanthanides were found to vary as a function of sample size.
3. The flame ionization detector response for $\text{Eu}(\text{HFA})_3 \cdot 2\text{TBP}$ and $\text{Tm}(\text{HFA})_3 \cdot 2\text{TBP}$ were found to vary by a factor of about two.

These observations indicate the need for further study of the gas chromatography of mixed-ligand complexes if it is hoped to develop the technique for practical application.

It is the purpose of this work to evaluate three different facets of the gas chromatography of mixed-ligand complexes:

1. Various mixed-ligand chemical systems.
2. Gas chromatographic columns.
3. Gas chromatographic detectors.

The objectives of each of these investigations will be discussed in turn. First, several mixed-ligand chemical systems have been evaluated to determine the gas chromatographic performance of different chemical combinations. Several mixed-ligand complexes which are easily extracted and thermally stable have been identified. An attempt has been made to draw some conclusions concerning the relationship between the composition of mixed-ligand complexes and optimum gas chroma-

tographic performance in regard to thermal stability and elution behavior.

A survey of different types of gas chromatographic columns has been carried out to determine which particular types of columns are most suited for determination of mixed-ligand complexes. More detailed studies of the most promising columns has shown something about the nature of the interaction between mixed-ligand complexes and gas chromatographic columns.

Finally, an evaluation of the response of the flame ionization detector and the thermal conductivity detector to mixed-ligand complexes has been made. This study has shown unusual response phenomena which need to be accounted for in the determination of mixed-ligand complexes by G.C.

In summary, this work will report an investigation of the basic facets of the gas chromatography of mixed-ligand complexes. It is hoped that the study will contribute to an understanding of the nature of this analytical procedure and to the development of insights which may be helpful for the further practical application of the technique.

III. AN INVESTIGATION OF THE DETERMINATION OF SEVERAL MIXED-LIGAND COMPLEXES BY GAS CHROMATOGRAPHY

A. Introduction

It is the purpose of these experiments to evaluate the gas chromatographic performance of several different mixed-ligand complexes. Butts (14) reported the apparent decomposition of some of the HHFA-TBP mixed-ligand complexes of the lanthanides during analysis by G.C. If mixed-ligand complexes are to be useful for analysis by G.C., the complexes should be stable under normal gas chromatographic conditions. Normal gas chromatographic conditions shall be taken to mean the existence of gas chromatographic instrumental parameters similar to those used for typical applications. This would imply column temperatures in the range of ambient to about 250°C and the use of common materials such as glass or stainless steel for column tubing and inlet liners. The stability of several different mixed-ligand complexes will be evaluated under normal gas chromatographic conditions. Thermal instability, or decomposition due to other factors, can be identified by observation of excessively skewed chromatograph peaks, the observation of multiple chromatograph peaks for a single complex, and by the presence of residue in the inlet liner after

determination of a complex.

Elution patterns for the mixed-ligand complexes will be evaluated in terms of retention time and chromatographic peak shape. Under normal gas chromatographic conditions, retention times should run no longer than 30 to 40 minutes. The gas chromatographic peaks should be sharp, have a reasonable width, and have little or no tailing and no leading edge. The gas chromatographic peak for the mixed-ligand complex should be easily resolved from the components of the extraction mixture.

The various mixed-ligand combinations which were studied will be discussed by reference to the individual β -diketones used. The most promising mixed-ligand combinations were studied in more detail and the data from these studies will be presented in the following discussion.

B. Experimental

1. Apparatus

a. Gas chromatographs Most of the gas chromatographic studies were performed on a Beckman GC-4 gas chromatograph equipped with an on-column inlet, flash-vaporization inlet, thermal conductivity detector, and dual hydrogen flame detector. The chromatograms were recorded with a Bristol model 560 Dynamaster recorder equipped with a Disc Integrator. Some

select experiments were run on a Hewlett-Packard Model 5756B equipped with a Hewlett-Packard Model 7128A recorder. High-purity helium supplied by the Matheson Company was used as a carrier gas.

b. Thermogravimetric analyzer A DuPont Model 950 thermogravimetric analyzer was used to obtain all thermograms.

c. Spectrophotometers A Cary Recording Spectrophotometer, Model 14, was used for visible spectra. A Beckman IR-7 infrared spectrophotometer was used to obtain infrared spectra.

d. Fluorimeter Fluorescence data were taken on an Aminco-Bowman Spectrophotofluorimeter equipped with a Moseley X-Y recorder.

e. pH meter All pH measurements were made on a Beckman, Model G, pH meter with a fiber-type saturated calomel reference electrode and a glass indicator electrode. The meter was standardized with Beckman pH standards.

f. Automatic shaker A Burrell Wrist-Action Shaker was used to shake solvent extraction mixtures.

2. Reagents

a. Lanthanides and yttrium The lanthanides and yttrium were obtained from Ames Laboratory stock as the oxides.

b. Thorium Thorium was obtained from reagent grade $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ from Fisher Scientific.

c. Uranium Reagent grade $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2) \cdot 2\text{H}_2\text{O}$ from Mallinckrodt Chemical Works was used as the source of uranium.

d. β -diketones The following β -diketones were prepared by John J. Richard, Ames Laboratory,¹ 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, H(FOD); 1,1,1,2,2,3,3,6,6,7,7,7-dodecafluoro-4,6-octanedione, H(DODEFOD); 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione, H(DECAFHD); 1,1,1,2,2,3,3-heptafluoro-7-methyl-4,6-octanedione, H(MFOD); 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, H(FHD). 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, H(HFA), and 1,1,1-trifluoro-2,4-pentanedione, H(TFA), were obtained from Peninsular Chem Research. The H(HFA) was redistilled at 66°C before use. 2,2,6,6-tetramethyl-3,5-heptanedione, H(THD), was obtained from Peninsular Chem Research and redistilled before use.

e. Neutral donors Tri-n-butylphosphate, TBP, was obtained from Fisher Scientific Company and purified by the procedure of Irving and Edgington (53), and Alcock et al. (2). Tri-n-butylphosphine oxide, TBPO, was obtained from Carlisle Chemical, and used after recrystallization. Di-n-butylsulfoxide, DBSO, was obtained from Crown Zellerback and used as received. Tri-n-octylphosphine oxide, TOPO, was obtained

¹The procedure of Springer, Meek and Sievers (130) was used, with some modification, for preparation of β -diketones.

from Eastman Kodak and used as received.

f. Solvents All solvents were reagent grade.

3. Techniques

a. Preparation of stock solutions of cations Solutions of the lanthanides and yttrium were prepared by dissolving 99.9% pure metal oxide in dilute HCl, evaporating to near dryness, and diluting to standard volume with NaOAc-HOAc buffer to pH ~5.5. Solutions of UO_2^{+2} were prepared by dissolving $\text{UO}_2(\text{OAc})_2$ in water and diluting to standard volume. An aqueous solution of thorium chloride was obtained by passing a solution of thorium obtained from $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ through a Dowex 1 x 8 ion exchange column in the chloride form.

b. Preparation of buffer solution About 27 grams of $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ was weighed into a one liter bottle and dissolved in one liter of distilled water. Hydrochloric acid was added as necessary to adjust the pH to 5.3 to 5.5.

c. Organic reagents Solutions of the β -diketones and neutral donors were prepared by weighing a specific β -diketone or neutral donor into a volumetric flask and then diluting to volume with the appropriate solvent.

d. Preparation of chelates Lanthanide chelates with H(FOD) were prepared according to the procedure of Springer, Meek and Sievers (130).

e. Procedure for solvent extraction The technique employed for the extraction of the complexes of the lanthanides and Y(III) was similar to that used by Carey (16). Two milliliter aliquots of 0.01 M lanthanide of Y(III) were placed in 15-ml glass stoppered centrifuge tubes. The aqueous solution of cation was contacted with 1.00 ml of 0.1 M β -diketone in cyclohexane and 1.00 ml of 0.05 M neutral donor in cyclohexane. In some cases, 4.00-ml of aqueous solution was used with 2.00-ml each of the β -diketone and neutral donor solutions. The mixtures were shaken one to three hours on a wrist action shaker. After shaking, the mixtures were centrifuged to aid in phase separation.

Extractions of UO_2^{+2} and Th(IV) were prepared by contacting 2.00-ml aliquots of aqueous UO_2^{+2} and/or Th(IV) with 2.00-ml aliquots of benzene which contained β -diketone in an amount five times the total metal concentration and neutral donor in an amount two times the total metal concentration. The mixtures were shaken one to three hours to establish equilibrium and centrifuged to achieve phase separation.

f. Sample injection Hamilton Microsyringes were used for all sample injections. All solvent extraction mixtures were sampled directly from the organic layer in the extraction tubes by syringe.

g. Sample collection There are numerous devices available for collection of the effluent from a gas chromatograph. For most of the trapping done in this study, a small diameter glass tube as reported by Armitage (4) was found to be adequate. A piece of glass tubing about four inches long with an outside diameter of three millimeters was flared at one end. This device could be placed either over the flame cone on the flame detector or on the exit line of the thermal conductivity detector. Complexes condensed in the cool end of the tube.

For the collection of some samples, a special device was fashioned. A stainless steel connector tube was fitted to the gas chromatographic column exit and extended through a small hole in the ceramic detector block on the Beckman G.C. 4. The end of the connector tube was fitted with an end cover which was bored to allow insertion of a small glass tube. A glass collection trap was designed which was a 1 1/2-inch x 1 1/2-mm tube topped by a 1/2-inch in diameter spherical glass bulb with a 1-inch x 5-mm tube opposite the small tube. The glass bulb was packed with glass wool. This device was found to trap mixed-ligand complexes very efficiently. Collected samples were washed from the collection tube or trap with a solvent which was compatible with the identification technique

to be employed.

4. Analytical determinations

a. Titration methods The stock solutions of the lanthanides and Y(III) were standardized with a standard solution of EDTA using Xylenol Orange as indicator (144). The EDTA was standardized with zinc. The UO_2^{+2} stock solution was standardized with standard EDTA using PAN indicator (64). For the UO_2^{+2} titrations, the normality of the EDTA was determined by titration of samples prepared from U_3O_8 . The Th(IV) stock solutions were standardized with EDTA using Xylenol Orange as indicator (144). For the Th(IV) titrations, the normality of the EDTA was determined by titration of samples prepared from $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$.

b. Mole ratio determinations For some of the mixed-ligand complexes of the lanthanides which had not been previously reported, it was considered necessary to verify the neutral donor content of the extracted complexes. The assumption that the metal to β -diketone ratio was 1:3 in the extracted species was considered justified on the basis of the work of other investigators (15,16,49,77,110,111,115,130,132,133). The determination of the neutral donor content was accomplished with a solvent extraction-molar ratio study similar to that employed by Carey (16, p. 103). The theory for

this type of study was discussed in Section I, LITERATURE REVIEW AND THEORY. Three lanthanides were used in each of the mole ratio studies - Er(III), Eu(III), and Nd(III). For each neutral donor evaluated, a series of extractions were made using varying concentrations of neutral donor. The extraction procedure discussed in the section above on techniques was used. After extraction, an aliquot of the organic phase of the Er(III) and Nd(III) extractions was analyzed in a 5-cm cell on the Cary Model 14 spectrophotometer according to the method of Taketatsu and Banks (133). The absorbance of the organic solution was measured at 520 nm for the erbium complexes and 584 nm for the neodymium complexes. The europium complexes were determined by measuring the apparent fluorescence of an aliquot of the organic phase of the extractions at 617 nm. The apparent activation wavelength was about 320 nm.

c. Identification of eluted species The method of collecting species eluted from the gas chromatograph was discussed in the section above on techniques. The samarium, europium, and terbium complexes could be identified by comparing the apparent fluorescence of samples eluted from the gas chromatograph to that of the organic phase of extraction mixtures. The apparent activation wavelength was about 320 nm.

The samarium, europium, and terbium complexes were identified by the apparent fluorescence at 565 and 600 nm, 617 nm, and 550 nm, respectively.

The stoichiometry of eluted complexes was determined by use of infrared spectroscopy. A quantitative infrared spectral determination of the ratio of neutral donor to β -diketone was performed on samples collected as eluted from the gas chromatograph. Solutions of known concentrations of neutral donor and β -diketone in carbon tetrachloride were prepared as standards. After infrared spectra were obtained for the standard solutions, the ratio of the absorbance of a selected stretching frequency of the neutral donor divided by the absorbance of a selected stretching frequency of the β -diketone was calculated. This ratio was plotted against the concentration ratio [neutral donor]/[ligand]. The relative concentration ratio of neutral donor to β -diketone in samples eluted from the gas chromatograph was determined from these standard curves. The specific stretching frequencies used for the determination of different β -diketone-neutral donor combinations are given in Table 3.1.

Table 3.1. Infrared spectral bands (cm^{-1}) for determination of [neutral donor]/[ligand] of collected gas chromatographic effluents

Ligand	Spectral band	Neutral donor	Spectral band	Absorbance ratio
H(FHD)	C-F stretch, 1127	TBP	C-H stretch, 2990	2990/1127
H(FHD)	C-F stretch, 1127	DBSO	C-H stretch, 2990	2990/1127
H(FHD)	C-F stretch, 1230	TBPO	C-H stretch, 2990	2990/1230
H(DODEFOD)	C-F stretch, 1127	TBP	P-O-R stretch, 1030	1020/1127
H(FOD)	C-F stretch, 1127	TBP	P-O-R stretch, 1030	1030/1127

C. Results and Discussion

1. 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione,
H(FOD)

The synthesis and application of H(FOD) by Springer, Meek, and Sievers (130) has been discussed in Section I, LITERATURE REVIEW AND THEORY. Sievers *et al.* (125) suggested that the steric crowding of the H(FOD) ligand upon chelation with the lanthanides completely restricts availability of the seventh and eighth coordination sites. This contention has been shown to be incorrect by Mitchell (77) who found the formation of mixed-ligand complexes of the lanthanides when extractions were performed using H(FOD) and TBP. Mitchell found diadduct complexes of Pr and Nd with H(FOD) and TBP while the study of Eu and Tm seemed to indicate the formation of mixtures of mono-adduct and diadduct complexes.

Unless noted otherwise, gas chromatographic conditions for the following studies are given in Table 3.2. Chromatograms for the determination of the mixed-ligand complexes of Eu and Nd with H(FOD) and TBP are shown in Figure 3.1. The chromatographic peaks for the mixed-ligand complexes of H(FOD) and TBP all exhibit very long leading edges as is illustrated in Figure 3.1. The chromatographic peak for the mixed-ligand

Table 3.2. Gas chromatographic conditions for determination of mixed-ligand complexes

Inlet temperature - 245°C
Inlet line temperature - 240°C
Inlet - Flash vaporization
Inlet liner - Borosilicate glass
Detector - Flame ionization
Detector temperature - 265°C
Detector line temperature - 260°C

complex of Er with H(FOD) and TBP was found to have a retention time of about 13 minutes with a leading edge beginning at 6 minutes, while the Tb complex was found to have a retention time of 17.5 minutes with a leading edge beginning at 8 minutes. These data were obtained under the same conditions as that shown in Figure 3.1. As is shown in Figure 3.1, the sample of Nd gave two gas chromatographic peaks for the complex. The retention times for the mixed-ligand complexes of the lanthanides with H(FOD) and TBP at 200°C on a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30 were in the range of about 13 to 20 minutes.

These data indicate that the mixed-ligand complexes of the lanthanides with H(FOD) and TBP are undergoing some decomposition during analysis by G.C. The exceptionally long leading edges observed for the gas chromatographic peaks of these complexes are indicative of deterioration of the solute

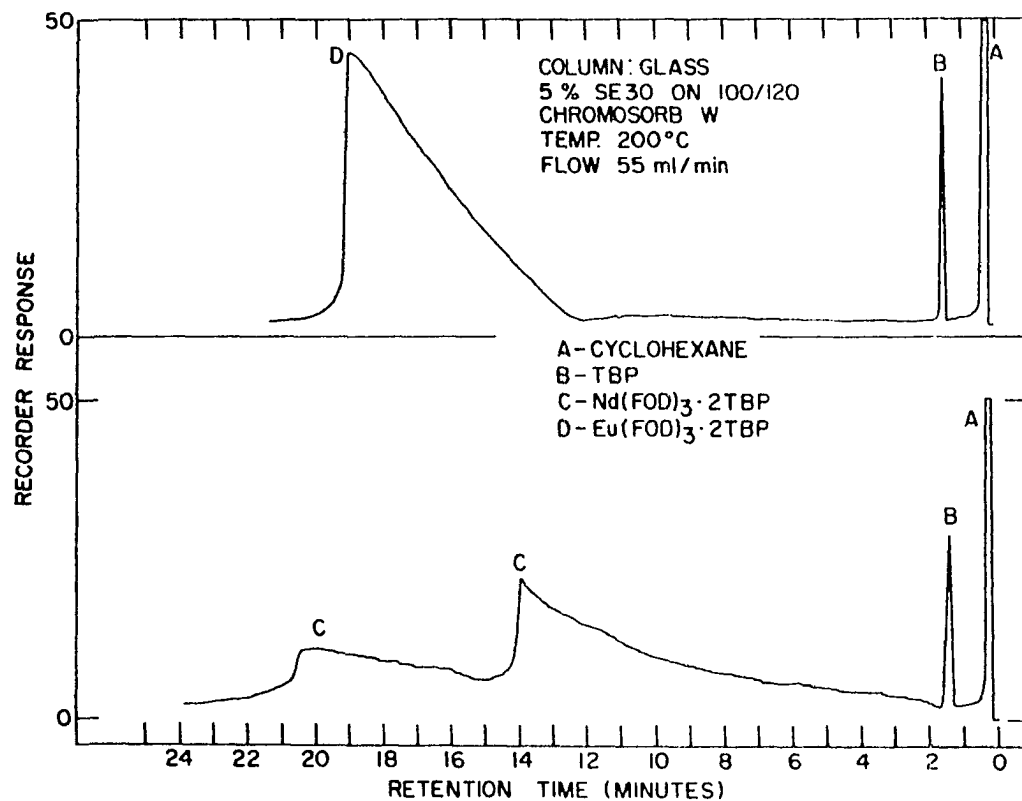


Figure 3.1. Gas chromatograms for mixed-ligand complexes of Eu and Nd with H(FOD) and TBP

elution band rather than column overloading which sometimes causes elution patterns with a leading edge. The observation of multiple peaks in the determination of the Nd complex also suggests that decomposition is occurring.

The long leading edge observed on the gas chromatographic peaks of these complexes could be due to gradual loss of TBP from the mixed-ligand complex as it traverses the column. It is likely that the TBP is not coordinated as strongly as it would be with a ligand which did not offer steric interference. Thus, the TBP could be dislodged from the complex as it is solubilized in the stationary phase of the GLC column. The resulting species would be more volatile and would contribute to a leading edge in the elution pattern.

A sharp elution pattern was observed for the $\text{Eu}(\text{FOD})_3 \cdot 2\text{TBP}$ complex at 180°C on a 4' x 1/4"-glass column packed with 80/100 mesh glass beads coated with 0.1% SE30. The short retention time of about 1.8 min indicates that there is very little partitioning of the complex on this column. Thus, this result does not contradict the argument given above for the poor elution behavior of these complexes on columns which partition better. The mixed-ligand complexes of $\text{H}(\text{FOD})$ and TBP appear to volatilize without decomposition in the injection port of the gas chromatograph. However, the data indi-

cate that these complexes are not stable for determination by G.C. on columns on which the complexes are partitioned.

2. 1,1,1-trifluoro-2,4-pentanedione, H(TFA)

The data from thermograms for mixed-ligand complexes of the lanthanides with H(TFA) and TBP reported by Mitchell (77) indicate that these complexes were both volatile and thermally stable. However, attempts to analyze these complexes by G.C. were not successful. Eu, Er, and Tb were extracted using H(TFA) and TBP. These elements were extracted quantitatively as reported by Mitchell, but no definable gas chromatographic peak was obtained for any of the complexes upon determination by G.C. of the organic phase. Spurious and highly skewed elution patterns were observed during the attempts to analyze the H(TFA)-TBP complexes.

It is apparent from these data that mixed-ligand complexes of the lanthanides using H(TFA) as the β -diketone are not suitable for analysis by G.C. Observation of spurious peaks in the elution pattern and failure to achieve a definable peak for the H(TFA) complexes suggest that these complexes are decomposing under normal gas chromatographic conditions.

3. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, H(HFA)

The determination by G.C. of the mixed-ligand complexes

of the lanthanides with H(HFA) and TBP has been reported by Butts and Banks (15). Figure 3.2 shows chromatograms for $\text{Eu(HFA)}_3 \cdot 2\text{DBSO}$ and $\text{Nd(HFA)}_3 \cdot 2\text{DBSO}$. For the study of the H(HFA)-DBSO complexes, the gas chromatographic detector was at 350°C , the detector line at 330°C , the inlet line at 300°C , and the liner at 265°C .

Sharp elution patterns were obtained for the Eu complex as can be seen in Figure 3.2. However, it was found that consecutive determinations of 0.01 M $\text{Eu(HFA)}_3 \cdot 2\text{DBSO}$ on a $4' \times 1/4''$ -glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30 gave peaks of decreasing size for the Eu complex. Table 3.3 lists the peak height vs sample number for a series of 3 microliter injections of the 0.01 M complex.

Table 3.3. Peak height for consecutive injections of 0.01 M $\text{Eu(HFA)}_3 \cdot 2\text{DBSO}$

Sample number	1	2	3	4	5	6	7	8
Peak height for complex	8.1	6.5	4.0	3.6	3.1	2.6	2.3	2.0

The chromatogram for $\text{Nd(HFA)}_3 \cdot 2\text{DBSO}$ shown in Figure 3.2 has a small unknown peak at a retention time of 2.5 min. The gas chromatographic peak for the Nd complex with a retention time of 3.8 min has a front shoulder and a leading edge.

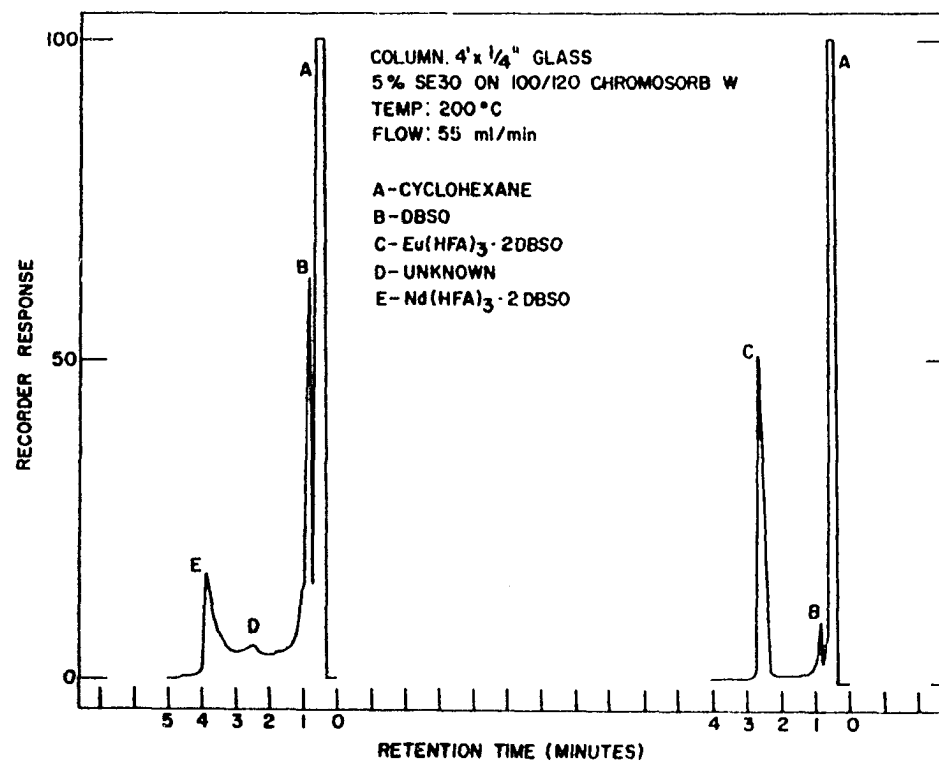


Figure 3.2. Gas chromatograms for $\text{Eu}(\text{HFA})_3 \cdot 2\text{DBSO}$ and $\text{Nd}(\text{HFA})_3 \cdot 2\text{DBSO}$

Attempts to obtain better elution patterns for the Nd complex were not successful.

These data indicate the existence of some instability in the HFA-DBSO complexes of the lanthanides. The Eu complex is either decomposing or being absorbed under normal gas chromatographic conditions, and unsatisfactory elution patterns were obtained for the Nd complex. Chromatograms obtained for the Er and Tb complexes of H(HFA) and DBSO were also of marginal quality.

4. 1,1,1,2,2,3,3-heptafluoro-7-methyl-4,6-octanedione, H(MFOD)

Mixed-ligand complexes of the lanthanides and yttrium with H(MFOD) and TBP were prepared by solvent extraction. These complexes were evaluated on a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30, and on a 4' x 1/4"-glass column packed with Chromosorb W coated with 1% ZE7. The determination of these mixed-complexes by G.C. was hindered by their lack of volatility. In order to obtain elution patterns for the complexes on the 5% SE30 column, column temperatures of 210°C to 235°C were required. Even under these conditions, poor elution patterns were obtained.

Figure 3.3 shows chromatograms for the Eu and Pr complexes as determined on the SE30 column. Both chromatograms

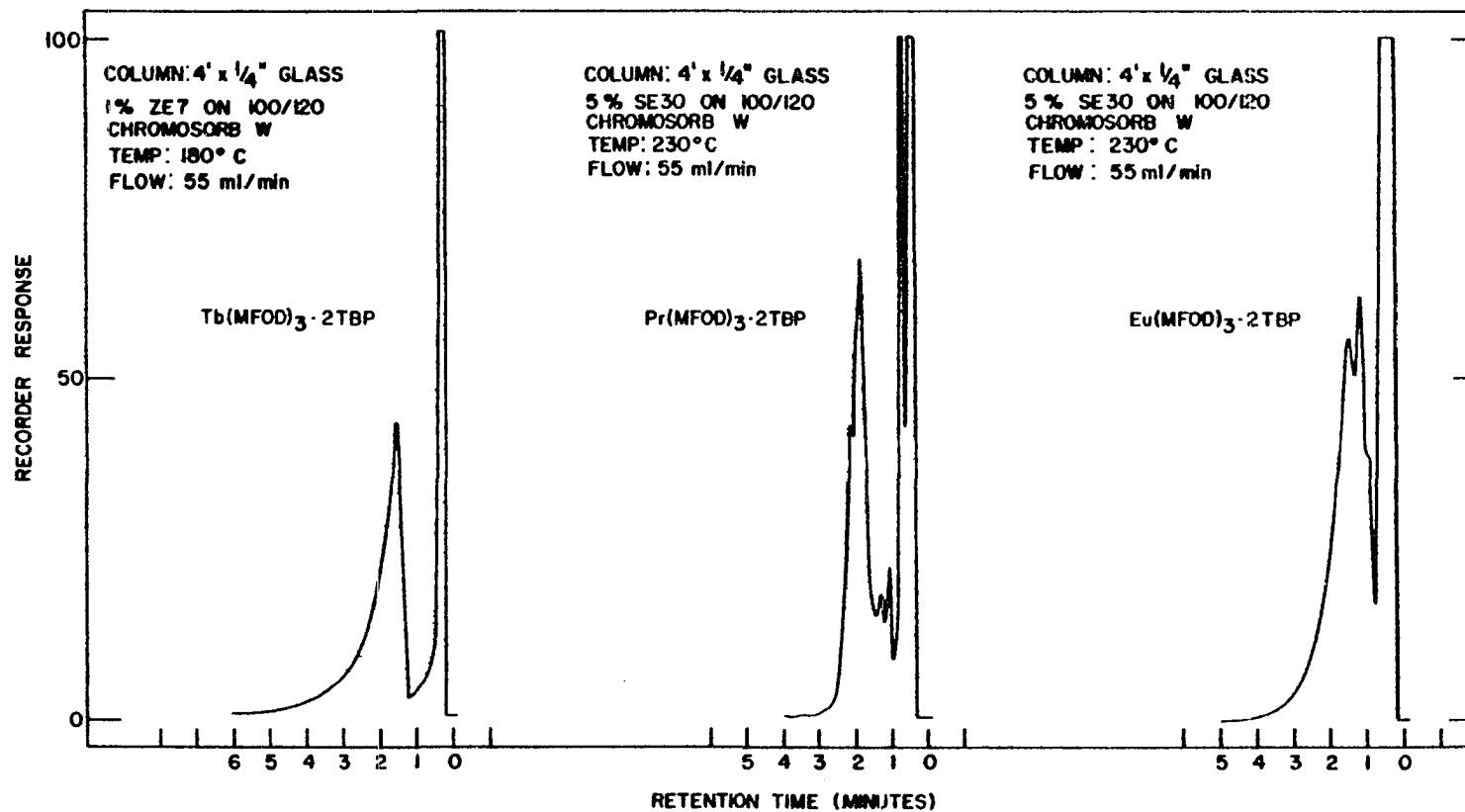


Figure 3.3. Gas chromatograms for mixed-ligand complexes of Eu, Pr, and Tb with H(MFOD) and TBP

have multiple peaks in the elution pattern. The existence of multiple peaks was characteristic of the chromatograms obtained for the H(MFOD)-TBP complexes. Since no other evidence of thermal decomposition was observed, such as residue on the injection port liner or increasing detector background levels, it is possible that the multiple peaks are due to column overloading. However, as can be seen in Figure 3.3, the gas chromatographic peaks are not well resolved from the solvent, and significant tailing is observed for both the Eu and the Tb complexes. The ZE7 column is a low resolution column which accounts for the fact that only one chromatographic peak is observed for the Tb complex on this column.

The high column temperatures required to obtain elution patterns for the H(MFOD)-TBP complexes and the peak tailing observed for these complexes both attest to the lack of sufficient volatility for these complexes to make them useful for the determination of the lanthanides by G.C.

5. 1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione,

H(DECAFHD)

Mixed-ligand complexes of the lanthanides with H(DECAFHD) and TBP were prepared by solvent extraction. Mitchell (77) has shown that the extracted mixed-ligand complexes have the following stoichiometry, $M(\text{DECAFHD})_3 \cdot 2\text{TBP}$ where M represents

the lanthanide ion.

Figure 3.4 shows chromatograms for $\text{Lu}(\text{DECAFHD})_3 \cdot 2\text{TBP}$, $\text{Dy}(\text{DECAFHD})_3 \cdot 2\text{TBP}$, $\text{Eu}(\text{DECAFHD})_3 \cdot 2\text{TBP}$, and $\text{Nd}(\text{DECAFHD})_3 \cdot 2\text{TBP}$. Excellent elution patterns were obtained for these complexes. The Lu, Dy, and Eu complexes were eluted at a column temperature of 190°C and the Nd complex at 200°C . All peaks in the elution pattern are identified. Of particular importance is the fact that the chromatographic peaks for the mixed-ligand complexes are very sharp and narrow with neither a leading edge nor tailing being observed for any of the complexes determined. This is in sharp contrast to the $\text{H}(\text{MFOD})\text{-TBP}$ complexes. An extensive study utilizing $\text{H}(\text{DECAFHD})$ was not carried out because only a small amount of the β -diketone was available. This ligand hydrated very easily and proved extremely difficult to synthesize. However, the results of the study with the available $\text{H}(\text{DECAFHD})$ indicated that β -diketones which have fully fluorinated side chains and are larger than $\text{H}(\text{HFA})$ should be evaluated. The next two ligands evaluated in this study are of this type.

6. 1,1,1,2,2,3,3,7,7,8,8,8-dodecafluoro-4,6-octanedione,

$\text{H}(\text{DODEFOD})$

The β -diketone $\text{H}(\text{DODEFOD})$ was investigated in detail because of the excellent results which were obtained with

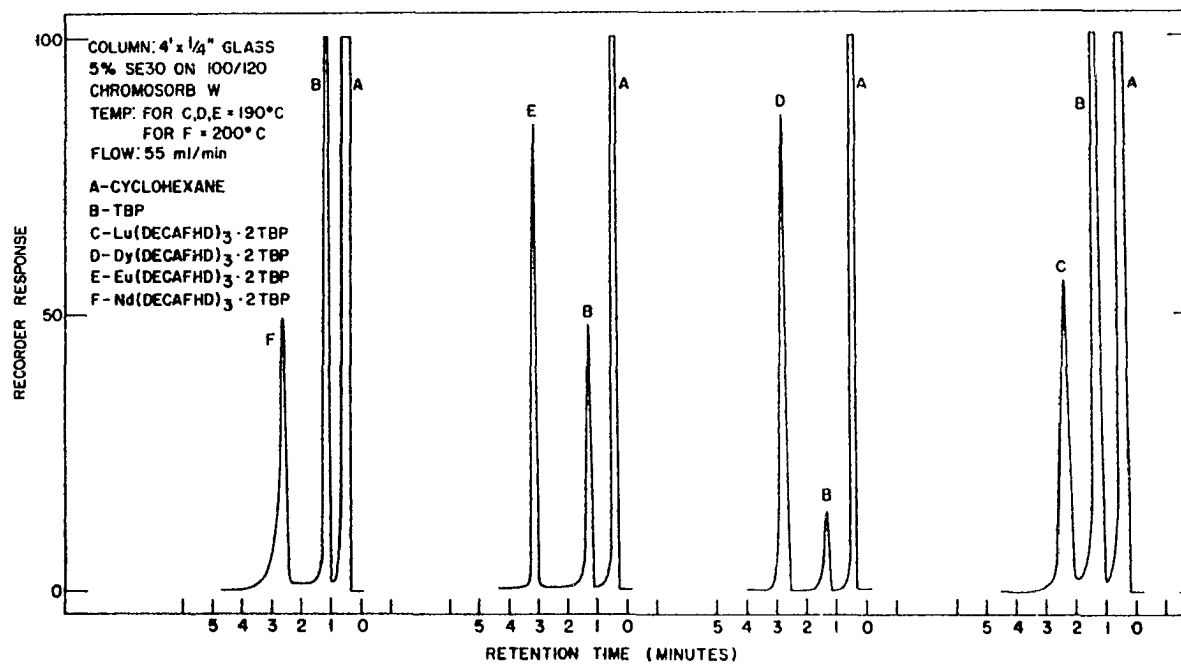


Figure 3.4. Gas chromatograms for mixed-ligand complexes of Lu, Dy, Eu and Nd with H(DECAFHD) and TBP

this ligand. H(DODEFOD) was used to form mixed-ligand complexes of the lanthanides with several different neutral donors. Table 3.4 lists the neutral donors which were evaluated.

Table 3.4. Neutral donors used with H(DODEFOD)

Tri- <u>n</u> -butylphosphate	TBP
Di- <u>n</u> -butylsulphoxide	DBSO
Tri- <u>n</u> -butylphosphine oxide	TBPO
Tri- <u>n</u> -octylphosphine oxide	TOPO
Dimethylsulphoxide	DMSO

Some thermal studies were performed to confirm the stability and volatility of the H(DODEFOD) complexes. Figure 3.5 shows thermograms for $\text{Er}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ and $\text{Eu}(\text{DODEFOD}) \cdot 2\text{DBSO}$. Both samples volatilized smoothly and completely indicating no decomposition during volatilization. The thermograms also suggest that the complexes may be determined by G.C. at 200°C or less. Thermograms were not obtained for all the H(DODEFOD) complexes of the lanthanides. When the solvent is stripped from these complexes, oils are formed. These oils are not easily purified to remove excess extraction reagents so that thermal data can be obtained on pure complex. In addition, it

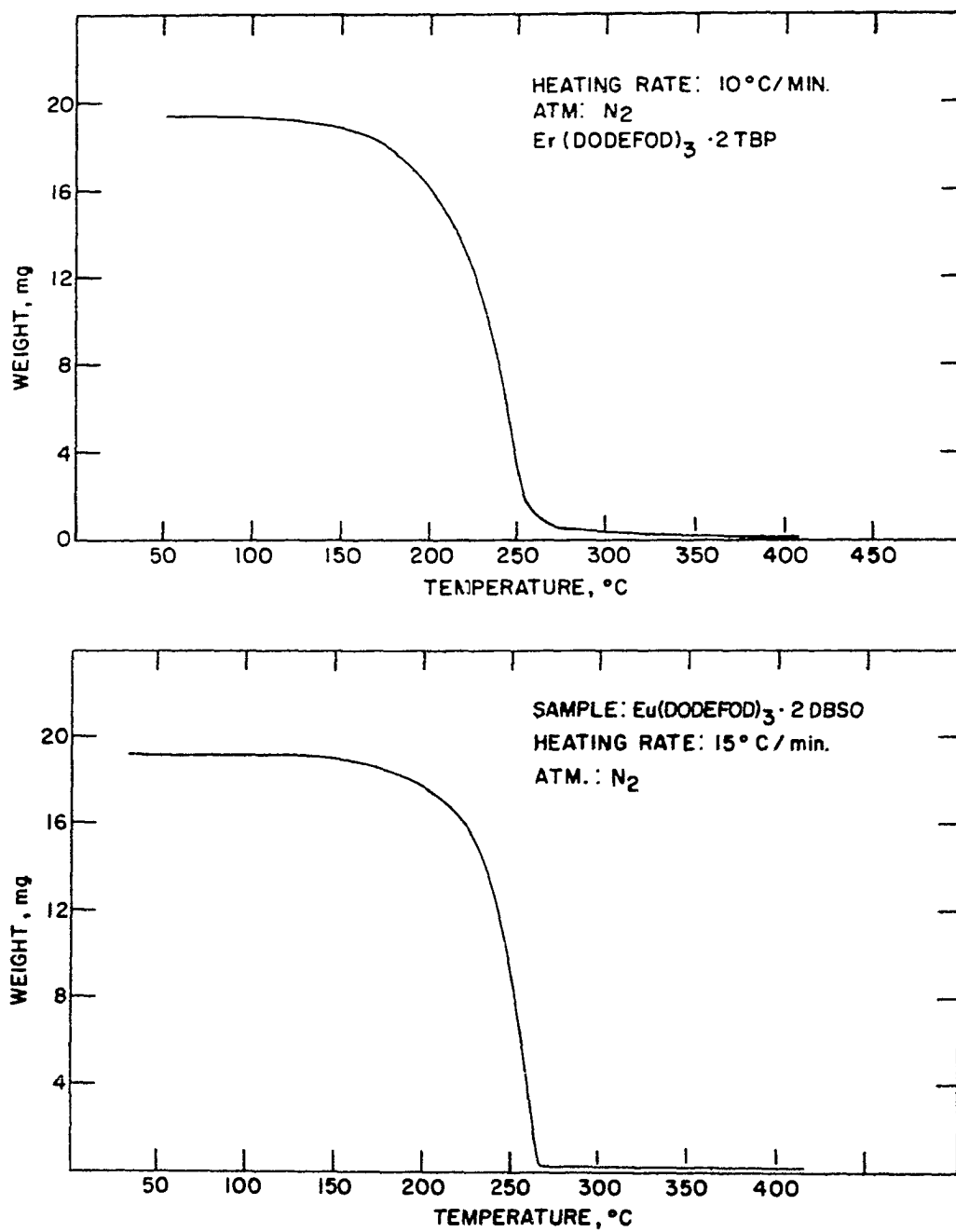


Figure 3.5. Thermograms for Eu(DODEFOD)·2DBSO and Er(DODEFOD)·2TBP

is not clear that the species which is formed in solvent extraction will be maintained when the solvent is stripped away. Hence, for the purposes of this study, it was of interest to know the nature of the species formed in the solvent extraction and whether or not this species is maintained during determination by G.C.

If the mixed-ligand complexes are to be determined quantitatively by G.C., the fate of the complex during analysis by G.C. must be known. It should be known whether the gas chromatographic peak attributed to the complex is due to the complex or to some fragment of the complex. Three different techniques were employed to identify the species eluted from the gas chromatograph in these studies: carbon-hydrogen analysis, fluorescence spectroscopy, and quantitative infrared spectroscopy. Details are given in the discussion of H(DODEFOD)-TPB.

a. H(DODEFOD)-TBP Mitchell (77) has shown the mixed-ligand complexes of the lanthanides with H(DODEFOD) and TBP to have a stoichiometry of $ML_3 \cdot 2Y$, where M is the metal ion, L is the β -diketone, and Y is the neutral donor. In this study, extractions of 0.01 M metal were prepared for the lanthanides and yttrium with H(DODEFOD) and TBP. Several experiments were performed to determine if the $ML_3 \cdot 2Y$ stoichiometry was main-

tained for these complexes during analysis by G.C.

To determine if the mixed-ligand complexes were being eluted from the gas chromatograph, a sample of $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ was trapped. Figure 3.6 shows apparent fluorescence spectra for a sample of the Eu complex taken directly from the organic phase in the extraction tube, and for the Eu complex trapped as eluted from the gas chromatograph. The spectra are identical. These data prove that the complex is being eluted from the gas chromatograph. However, the fluorescence data are not sufficient to prove the composition of the complex eluted from the gas chromatograph. A fluorescence spectrum would be obtained for $\text{Eu}(\text{DODEFOD})_3$ if it were eluted after losing the TBP during the analysis. Hence, further data are needed to prove the stoichiometry of the eluted complex.

Carbon-hydrogen analysis can be employed to analyze samples trapped from a gas chromatograph. Table 3.5 shows the results obtained for a carbon-hydrogen analysis of a sample of $\text{Pr}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ which was trapped as eluted from the gas chromatograph. Samples about three milligrams in size were used for the determination. Although these data tend to indicate that the $\text{Pr}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ complex was eluted from the gas chromatograph without decomposition, larger sample sizes would be needed to obtain accurate results.

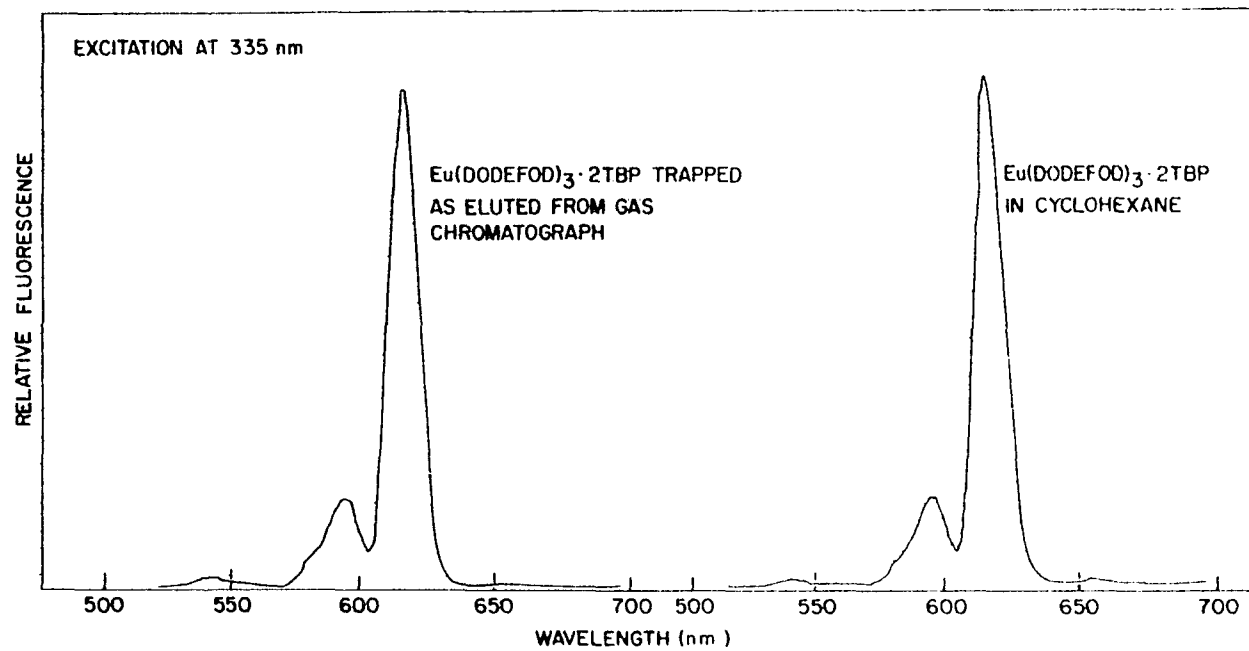


Figure 3.6. Apparent fluorescence spectra for $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{TBP}$

Table 3.5. Carbon-hydrogen analysis of Pr(DODEFOD)·2TBP collected as eluted from the G.C.

	Theory	Found
C	32.99	34.55
H	2.6	3.6

Three to four hours effort was required in order to obtain enough complex for one carbon-hydrogen analysis. In view of this difficulty in obtaining enough material from the G.C. to do carbon-hydrogen analysis, a quantitative infrared spectrophotometric technique was developed to determine the stoichiometry of the complexes eluted from the gas chromatograph. The details of this procedure have been discussed in the section above on Analytical Determinations.

Figure 3.7 shows infrared spectra for H(DODEFOD) in CCl₄ solution and for a sample of Pr(DODEFOD)₃·2TBP which was trapped as eluted from the gas chromatograph. The infrared spectra of DBSO in CCl₄ and of TBP in CCl₄ solution are shown in Figure 3.8. Assignments for the major infrared spectral bands of H(DODEFOD) and TBP are given in Table 3.6. These assignments agree with those reported in the literature for fluorinated β-diketones and TBP (10,34,35,36,66,84,96,97).

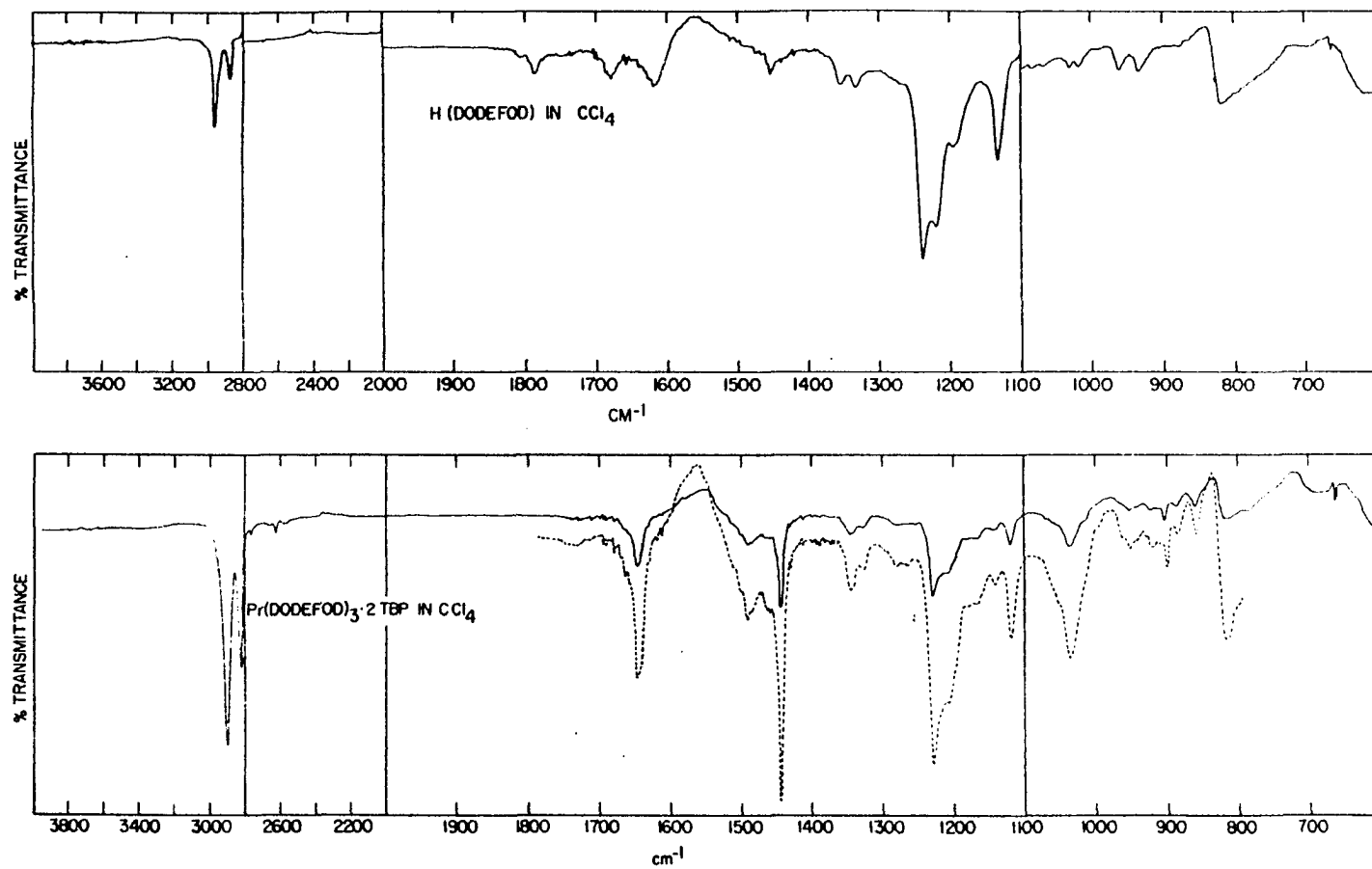


Figure 3.7. Infrared spectra of H(DODEFOD) and Pr(DODEFOD)₃·2TBP

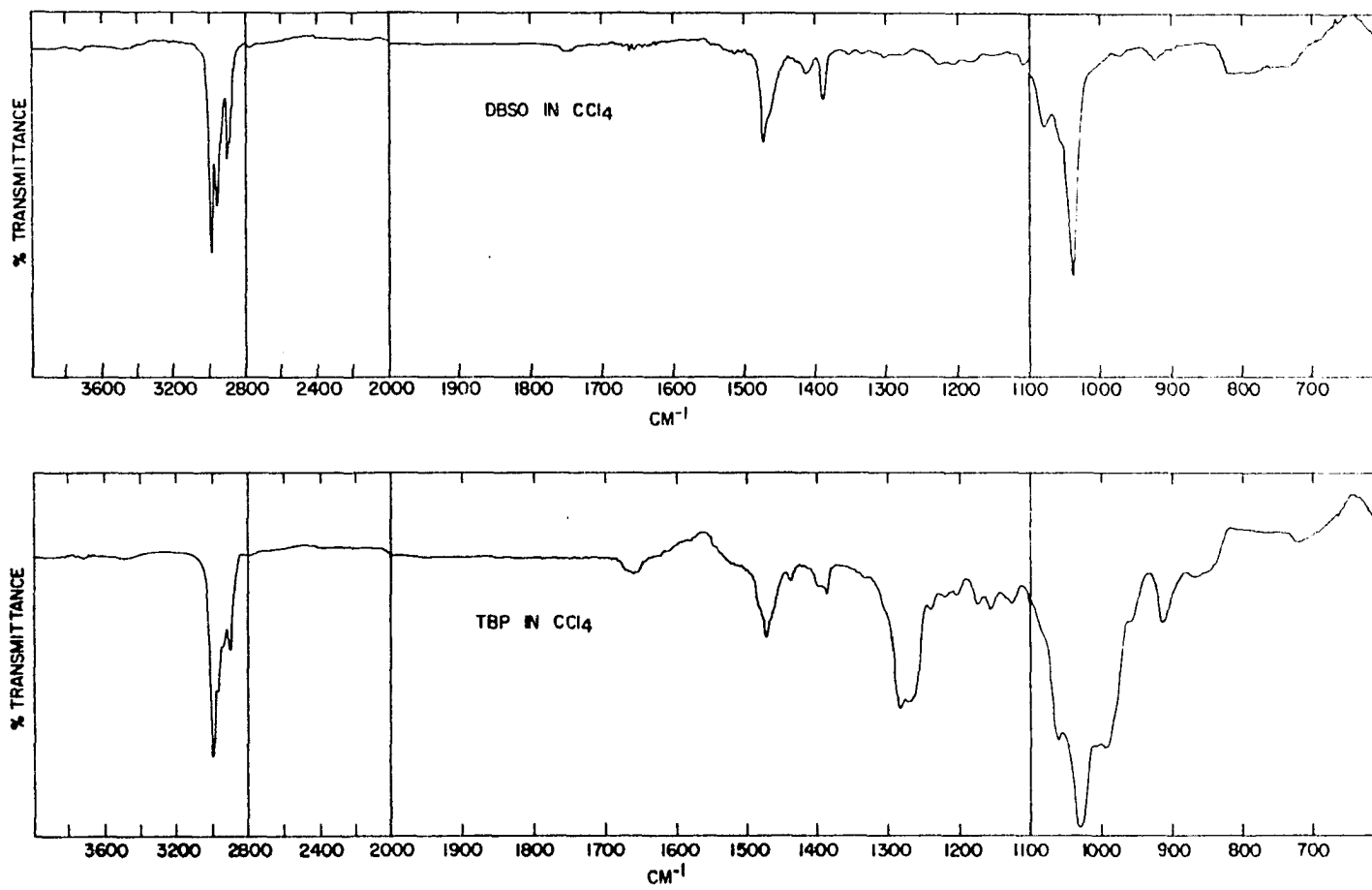


Figure 3.8. Infrared spectra of TBP and DBSO

Table 3.6. Assignment of infrared spectral bands (cm^{-1}) for H(DODEFOD), H(FHD), TBP, DBSO and TBPO

Assignment	H(DODEFOD)	H(FHD)	TBP	DBSO	TBPO
CH str.	2960 2870		2990	2990	2990
			2965	2965	2965
			2930	2930	2930
			2900	2900	2900
C=O str. } C=C str. } C...C and } C...O str. }	1678 1617	1680 1620			
CH bend	1454		1455	1460	1460
C=O str.	1354	1333			
P=O str.			1285		1223
			1268		1174
C-F str.	1238 1217 1188 1127	1230 1211 1185 1127			
[P-O]-R str.			1060		
			1030		
			990		
S=O str.				1080	
				1060	
				1036	
C-H out of plane bend	965	995	910		966

The standard curve used to obtain the amount of TBP compared to the amount of β -diketone present in samples collected from the gas chromatograph is shown in Figure 3.9. The curve was obtained by plotting the ratio of the absorbance of the [P-O]-R band at 1030 cm^{-1} from the TBP to the absorbance of the C-F band at 1127 cm^{-1} from the β -diketone versus the relative concentration ratio $[\text{TBP}]/[\beta\text{-diketone}]$. The standard curve indicates that a ratio of absorbances from 0.95 to 1.63 implies a ratio of neutral donor to ligand in the range 1.5/3 to 2.5/3.

Selected mixed-ligand complexes of the lanthanides with H(DODEFOD) and TBP were collected as eluted from the gas chromatograph. Infrared spectra were obtained for each of the collected samples, as example being illustrated by the spectrum shown for $\text{Pr}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ in Figure 3.8. The solid line shown for the spectrum of the Pr complex represents the spectrum obtained with normal operation of the infrared instrument, while the dotted line indicates the spectrum obtained with scale expansion which allowed more precise measurement of the absorbance ratios.

Table 3.7 shows the results of the quantitative infrared study. These data indicate that the absorbance ratios for

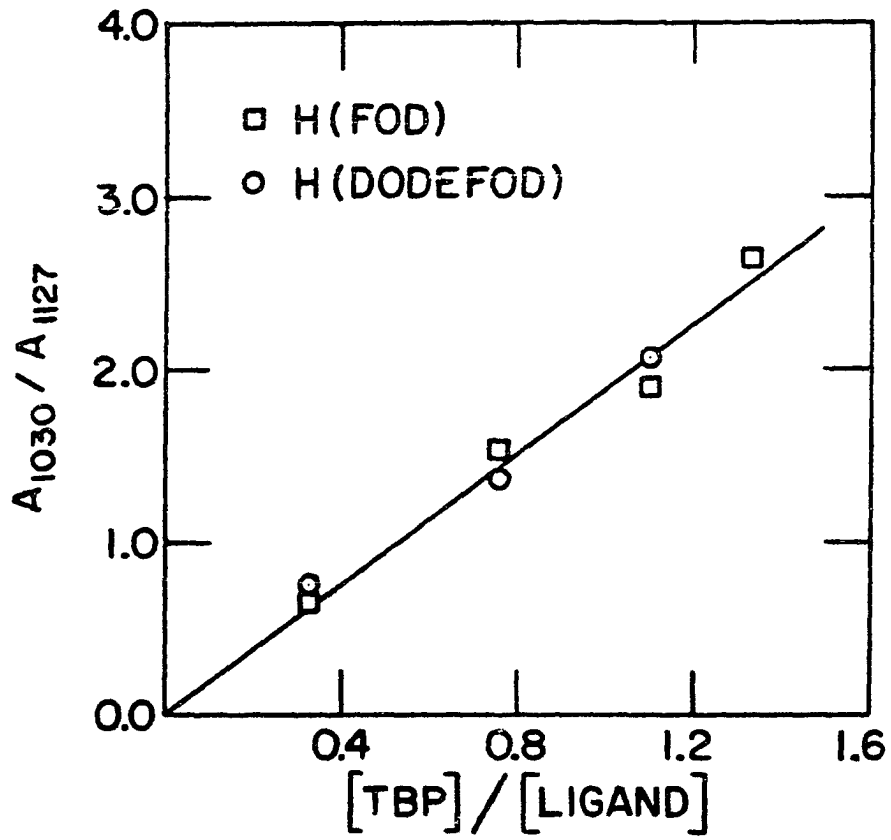


Figure 3.9. Calibration curve relating absorbance ratio to the ratio of TBP to ligand

Table 3.7. Ratios of the absorbance of the [P-O]-R band at 1030 cm^{-1} to the absorbance of the C-F band at 1127 cm^{-1} for mixed-ligand complexes of H(DODEFOD) and TBP

Complexes	A_{1030}/A_{1127}
Lu	1.22
Yb	1.28
Er	1.17
Ho	1.38
Tb	1.43
Nd	1.61
Pr	1.62
Y	1.42

the complexes which were collected all fall in the range 0.95 to 1.63 indicating a stoichiometry of $ML_3 \cdot 2Y$ for the complexes of the lanthanides with H(DODEFOD) and TBP when these complexes are eluted from the G.C. Thus it is confirmed that the stoichiometry of the species eluted from the gas chromatograph is the same as that of the species formed in the solvent extraction.

Shown in Figure 3.10 are gas chromatographic peaks obtained for the DODEFOD-TBP complexes with the lanthanides and yttrium. The chromatograms from which these peaks were taken were obtained using a 4' x 1/4" glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30. The column temperature was 190°C except for the determination of the

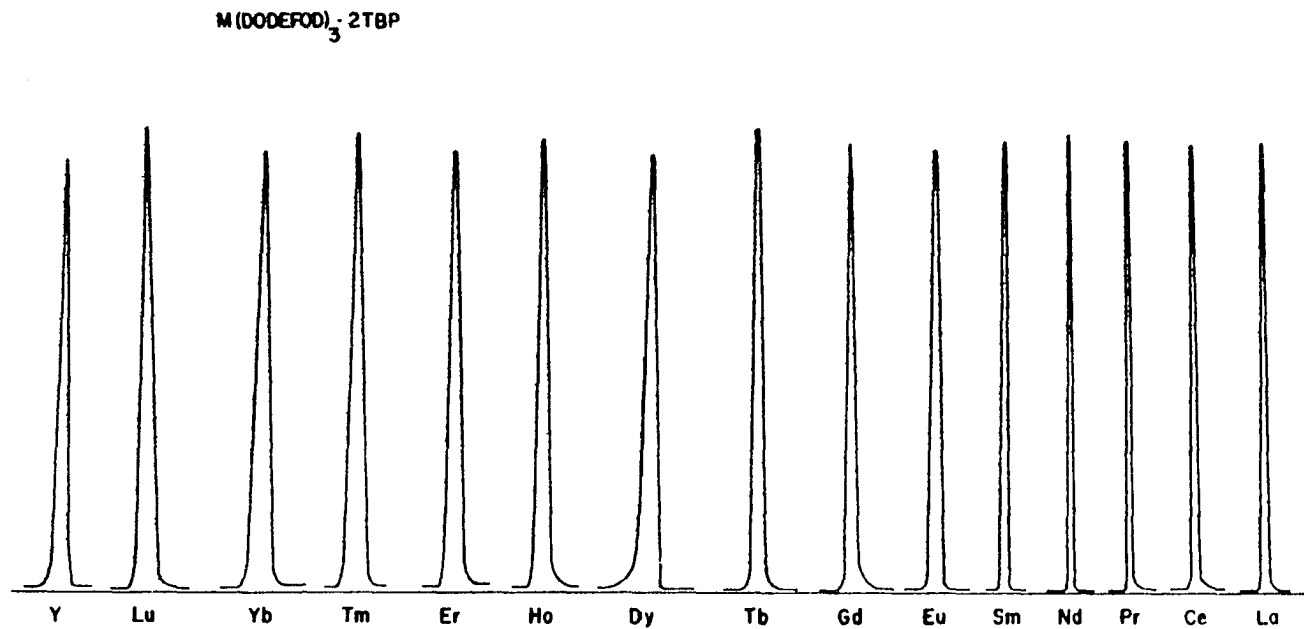


Figure 3.10. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(DODEFOD) and TBP

complexes of Nd, Pr, Ce, and La which were determined at a column temperature of 200°C. The chromatographic peaks obtained for these complexes are all sharp with no tailing and no leading edges. Retention time for the complexes ranged from about 2.5 min to 4.5 min indicating that the complexes were quite volatile.

The data which indicate the stoichiometry of the eluted complexes and the data for the determinations by G.C. demonstrate that the mixed-ligand complexes with H(DODEFOD) and TBP are thermally stable, volatile, and that the complexes yield excellent elution patterns. Clearly these complexes can be used for the determination of the lanthanides by G.C.

b. H(DODEFOD)-DBSO During the study of the β -diketone H(DODEFOD), it was learned that the ligand could not be reasonably obtained pure. Even with precipitation of the ligand as the copper chelate, three to five percent of some impurity remained. Evidence of the impurity is seen in the infrared spectra shown in Figure 3.7. Bands of moderate intensity are seen in the 2900 cm^{-1} (C-H stretch) region. If the H(DODEFOD) were pure, there should be very little absorption in this region. However, since the study of DODEFOD-TBP complexes gave no indication of interference arising from

this impurity in the ligand, it was decided to continue the evaluation of this ligand with other neutral donors.

Extractions of 0.01 M metal were prepared for the lanthanides and yttrium with H(DODEFOD) and DBSO. Samples of each were determined by G.C. on a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30. Figure 3.11 shows chromatographic peaks which were obtained for the DODEFOD-DBSO complexes. All the complexes were determined at a column temperature of 200°C except for the complexes of Nd, Pr, Ce, and La which were determined at 210°C.

Excellent elution patterns were obtained for the DODEFOD-DBSO complexes as can be seen in Figure 3.11. No leading edges or peak tailing is observed for the chromatographic peaks obtained for these complexes and the peaks are sharp without excessive peak width. These data indicate that the mixed-ligand complexes of the lanthanides with H(DODEFOD) and DBSO can also be used to determine the lanthanides by G.C.

Figure 3.12 shows chromatograms for the determination of $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{DBSO}$ on two different gas chromatographic columns. A significant difference in partition behavior is observed for the mixed-ligand complex on these different columns. The column using ZE7 as a stationary phase exhibits

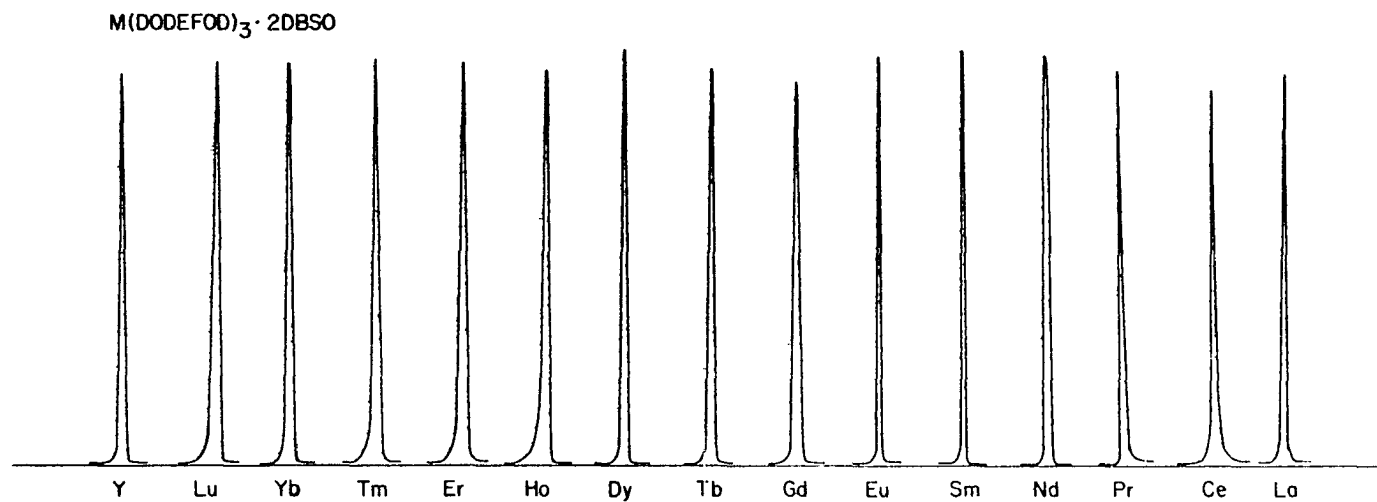


Figure 3.11. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(DODEFOD) and DBSO

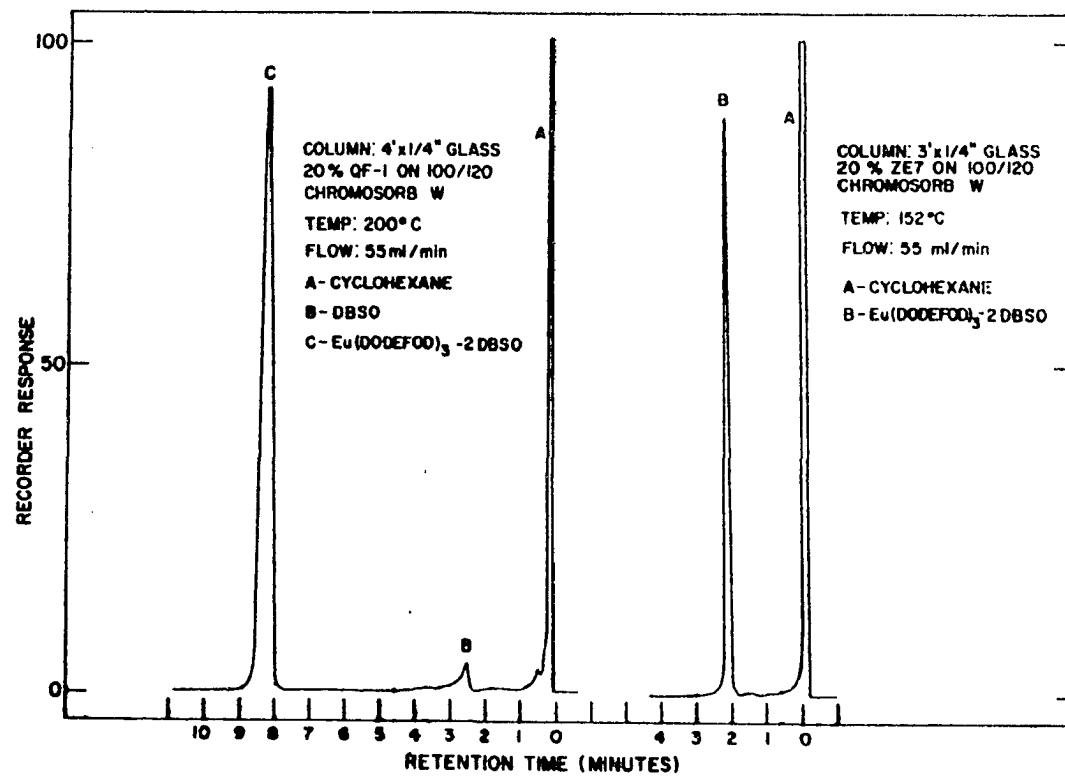


Figure 3.12. Gas chromatograms for $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{DBSO}$

very little resolution of the components of the extraction mixtures. As a result the complex is eluted quickly and at a very low temperature, but with little resolution from the solvent of the extraction mixture. The column using QF-1 as a stationary phase exhibits much more retention of the complex. In the determination using the QF-1 column, the complex is retained for a much longer period than was the case with the ZE7 column even though the column temperature for the QF-1 column was 48°C higher. Resolution of the Eu complex from the components of the solvent extraction mixture is much better with the QF-1 column.

It is important to note that sharp elution patterns were obtained for the $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{DBSO}$ complex on both columns. These data demonstrate the fact that the retention of mixed-ligand complexes can be varied by utilization of different stationary phases in the GLC column. This is an important first step in the effort to achieve resolution of more complicated systems. A more complete discussion of the partitioning of mixed-ligand complexes will be given in Section IV of this thesis.

c. H(DODEFOD)-TBPO Butts (14) attempted to determine the mixed-ligand complexes of the lanthanides with H(HFA) and TBPO by G.C. and reported that the complexes decomposed.

However, it was anticipated that the mixed-ligand complexes using TBPO as the neutral donor would extract well, so extractions with H(DODEFOD)-TBPO were studied. Extractions of 0.01 M Lu, Er, Tb, Eu, Sm, and Nd were prepared using H(DODEFOD) and TBPO. The color of the organic phase in the extractions of Er and Nd, and the fluorescence under a uv light of the organic phase in the case of Tb, Eu, and Sm indicated that solvent extraction of the DODEFOD-TBPO complexes did occur.

Figure 3.13 shows chromatograms for $\text{Er}(\text{DODEFOD})_3 \cdot 2\text{TBPO}$ and $\text{Tb}(\text{DODEFOD})_3 \cdot 2\text{TBPO}$. These chromatograms are not of especially good quality. The chromatographic peak for the Er complex is somewhat distorted and apparently on top of the tailing portion of the TBPO peak. Multiple peaks are observed for the Tb complex and peak distortion or multiple peaks were also observed for the other complexes of DODEFOD-TBPO.

At the time these data were taken, these poor chromatographic results were interpreted to mean that the DODEFOD-TBPO complexes were unstable and decomposed during determination by G.C. However, later work revealed that these irregular elution patterns are the result of severe column over-

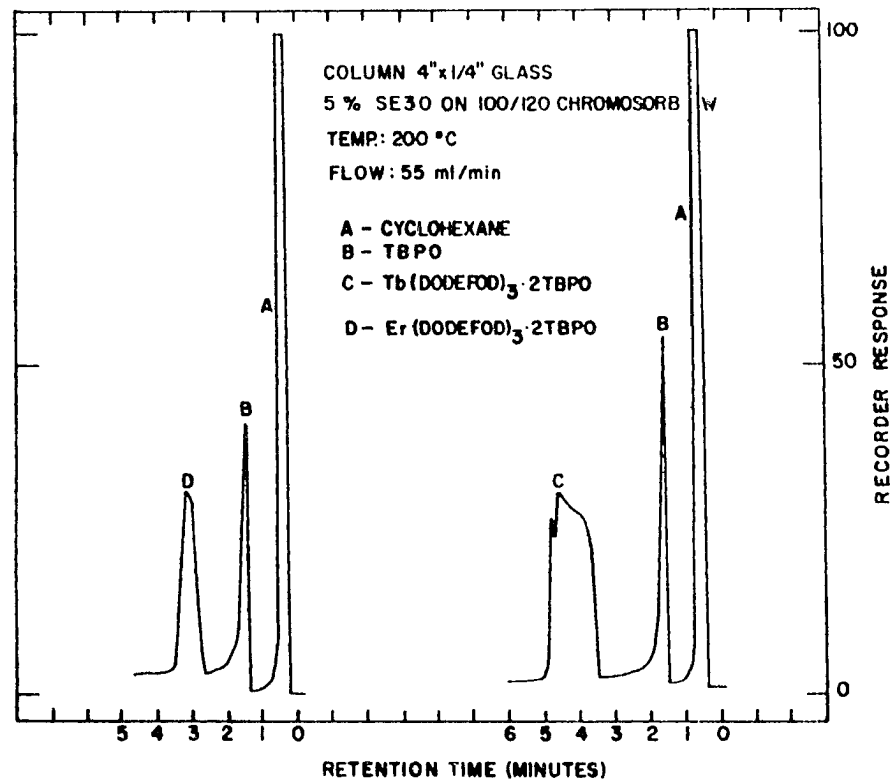


Figure 3.13. Gas chromatograms for the mixed-ligand complexes of Eu and Tb with H(DODEFOD) and TBPO

loading and not decomposition of the complexes. A detailed discussion of this column overloading is given in Section IV.

The data obtained in this work indicate that DODEFOD-TBPO complexes of the lanthanides are volatile and thermally stable and that they can be determined by G.C. Because of the problem of overloading the GLC column while determining these complexes, small sample sizes must be used to obtain reasonable results.

d. H(DODEFOD)-DMSO Solutions 0.01 M in Lu, Er, Eu, and Sm were extracted using cyclohexane solutions of H(DODEFOD) and DMSO. The pink color of the cyclohexane phase in the case of Er and the fluorescence under uv light of the cyclohexane phase in the cases of Sm and Eu indicated that the lanthanides did extract. Figure 3.14 shows a chromatogram for the Eu-DODEFOD-DMSO complex. This chromatogram is typical of the elution patterns observed for the determination by G.C. of the mixed-ligand complexes of H(DODEFOD) and DMSO. Multiple peaks were observed for all the complexes determined. The elution patterns varied significantly from run to run indicating that the complexes of DODEFOD-DMSO were decomposing during analysis. An increase in background noise, which is also an indication of decomposition, was observed after several determinations of the DODEFOD-DMSO complexes. Because

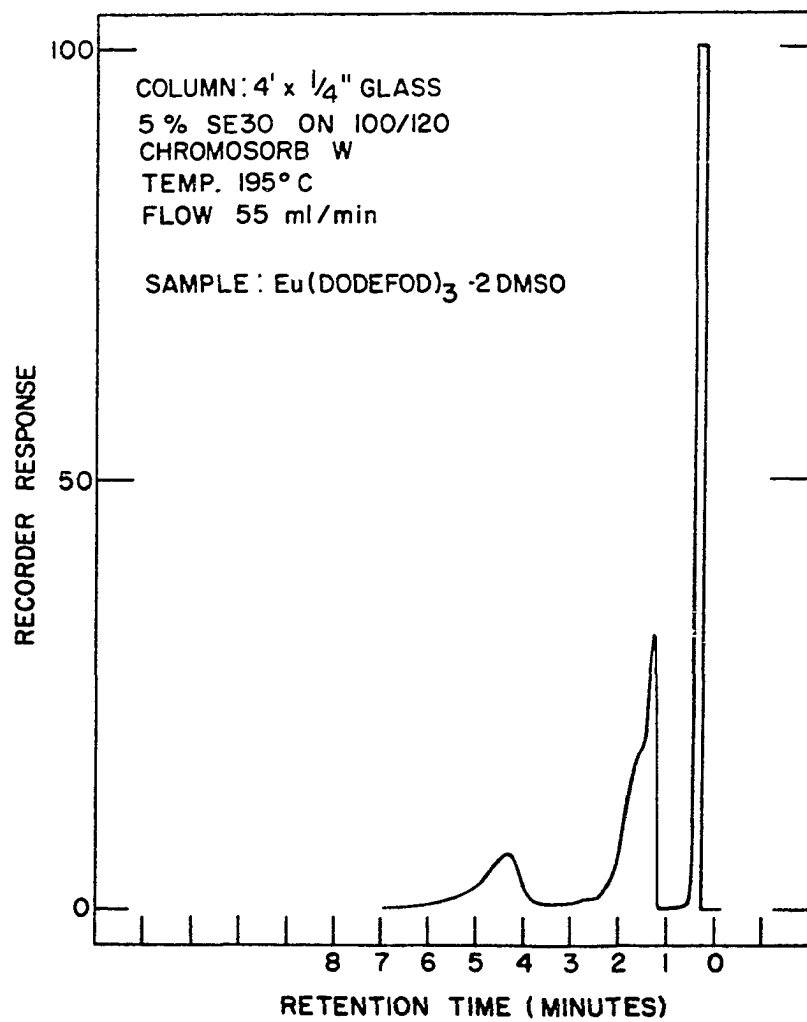


Figure 3.14. Gas chromatogram for the mixed-ligand complex of Eu with H(DODEFOD) and DMSO

of the background noise, the detector was heated to 345°C, the detector line to 330°C, and inlet line to 300°C for these determinations.

These data indicate that the DODEFOD-DMSO complexes of the lanthanides are not suited for determination by G.C. It is apparent that the DODEFOD-DMSO complexes are not stable and decompose during analysis by G.C.

e. H(DODEFOD)-TOPO Solutions 0.01 M in Er, Tb, and Eu were extracted using H(DODEFOD) and TOPO. The pink color of the cyclohexane phase in the case of Er and the fluorescence of the organic layer of the extractions of Tb and Eu indicated that complexes of these metals were extracted. Several attempts were made to determine the DODEFOD-TOPO complexes by G.C. No identifiable chromatographic peaks were observed for these mixed-ligand complexes on a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30, or on a 4' x 1/4"-glass column packed with 80/100 mesh glass beads coated with 0.1% SE30. Column temperatures as high as 250°C were used.

No specific evidence was observed which indicated that the DODEFOD-TOPO complexes were decomposing during analysis. $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{TOPO}$ has a formula weight of about 2000. It is possible that these complexes are stable, but not volatile

under normal gas chromatographic conditions. In any case, these data indicate that the DODEFOD-TOPO complexes of the lanthanides are not suitable for determination by G.C.

7. 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, H(FHD)

The β -diketone H(FHD) was synthesized with anticipation that it could be obtained pure, and that it would give excellent gas chromatographic results as did H(DODEFOD). This anticipation proved to be correct on both counts, so a detailed study was undertaken with this ligand. Work by Schweitzer et al. (107) on the volatilities of some lead β -diketonates is the only known reference to the synthesis and use of H(FHD). Thus this study appears to be a new application of this ligand.

As was pointed out in the discussion of H(DODEFOD), it is important in the case of mixed-ligand complexes which are to be used for determination of metals by G.C. to know the nature of the species formed in the solvent and whether this species is maintained during analysis by G.C.

Since the extraction of mixed-ligand complexes using H(FHD) as the β -diketone have not been studied, it was necessary to do some extraction studies with H(FHD) and the neutral donors of interest, TBP, DBSO, and TBPO, to determine the nature of the species formed in the solvent extraction of

the lanthanides. The theoretical background for the solvent extraction techniques used here was given in Section I, and the details of the procedure are given in the beginning of Section III in the discussion on Analytical Determinations. Data for the extraction studies, for the identification of species eluted from the gas chromatograph, and for the elution patterns obtained for the mixed-ligand complexes are given in the following discussion.

Figure 3.15 shows examples of the absorption spectra which were used to determine the mixed-ligand complexes of Er. These spectra exhibit no change as a function of the neutral donor involved. Identical spectra were also obtained for the different mixed-ligand complexes of Nd as is shown in Figure 3.16. An example of the apparent fluorescence spectra used to determine the Eu complexes is shown in Figure 3.17.

a. H(FHD)-TBP The extraction of selected lanthanides into cyclohexane containing a constant amount of H(FHD) and varying molar ratios of TBP to metal ion was studied. The molar ratio data reported in Figure 3.18 show the formation of the diadduct complex. There is some scatter in the data for the extraction of europium as a result of inaccuracy in the sampling of the organic phase of the extraction mixture. It

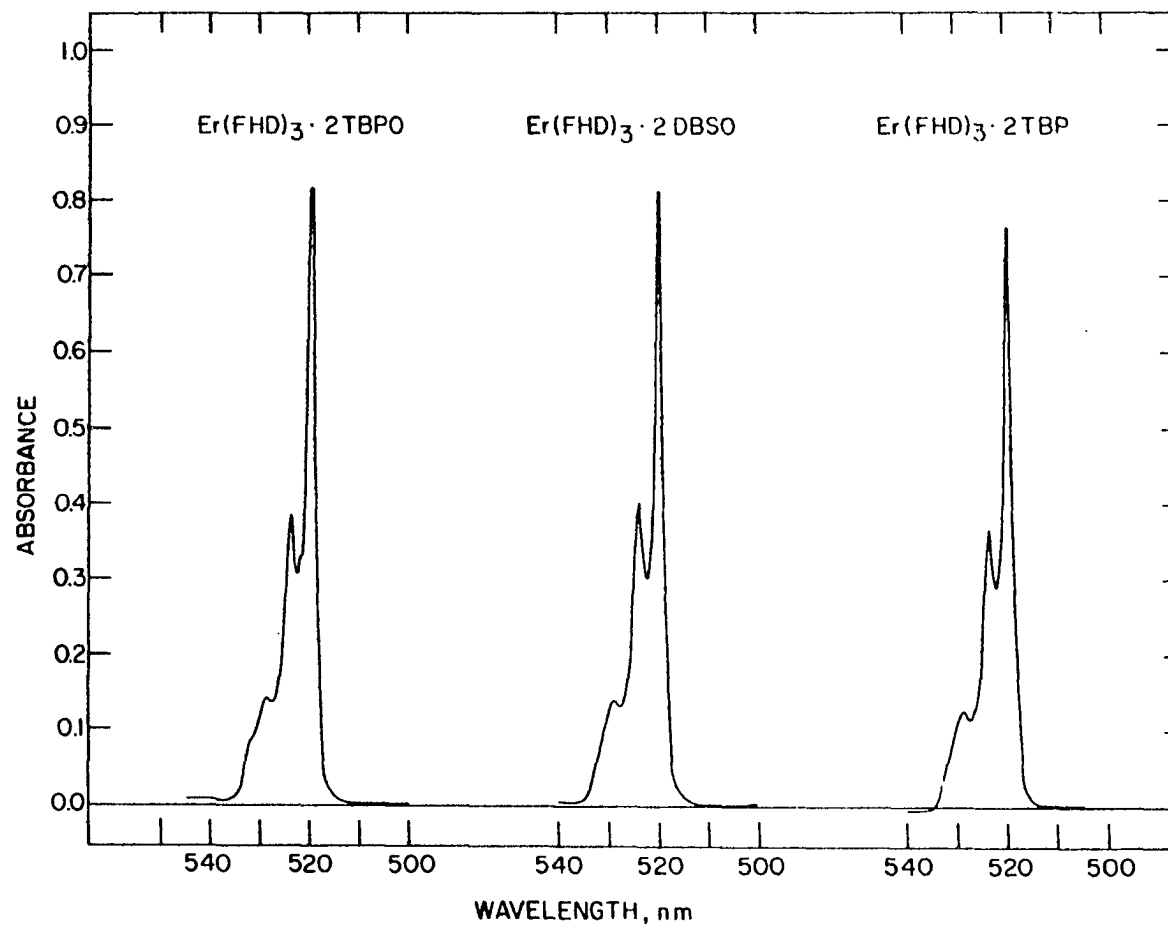


Figure 3.15. Absorption spectra for cyclohexane solutions of Er(FHD)₃ · 2TBPO, Er(FHD)₃ · 2DBSO, and Er(FHD)₃ · 2TBP

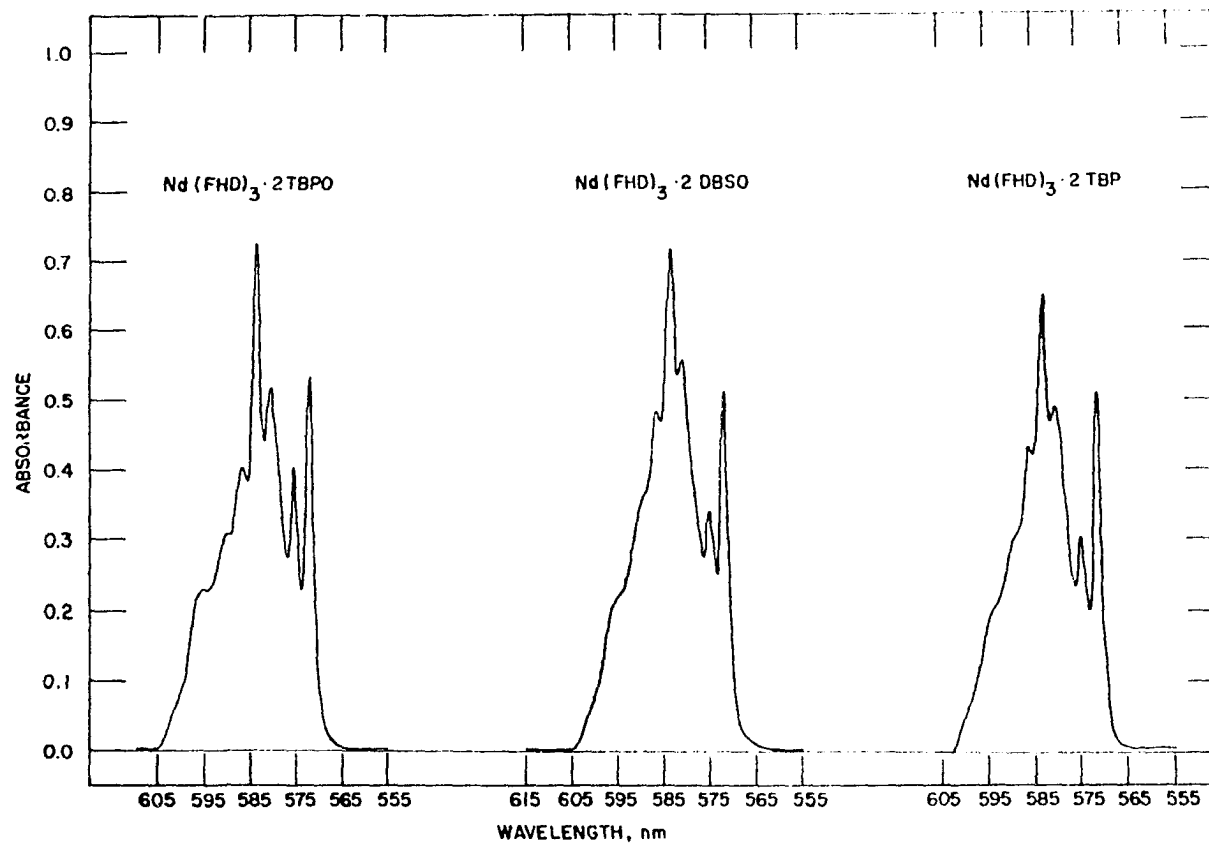


Figure 3.16. Absorption spectra for cyclohexane solutions of $\text{Nd}(\text{FHD})_3 \cdot 2\text{TBPO}$, $\text{Nd}(\text{FHD})_3 \cdot 2\text{DBSO}$, and $\text{Nd}(\text{FHD})_3 \cdot 2\text{TBP}$

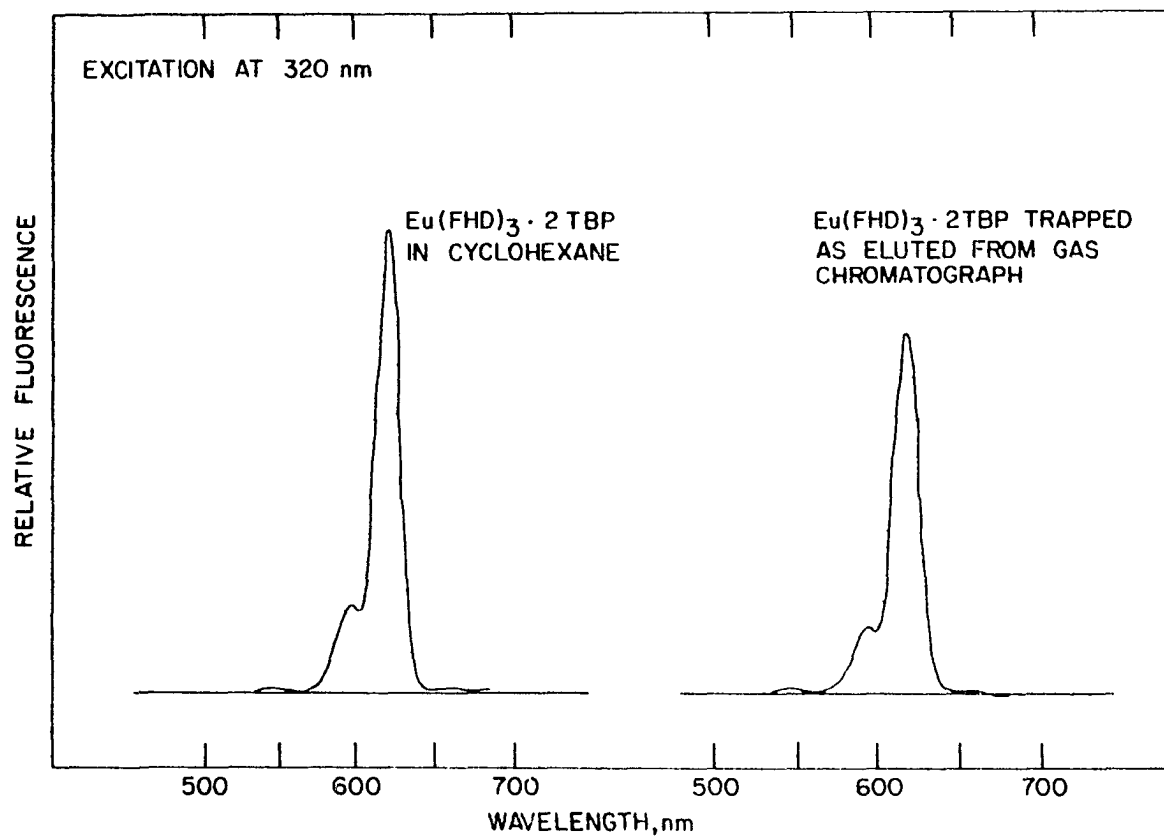


Figure 3.17. Apparent fluorescence spectra for $\text{Eu}(\text{FHD})_3 \cdot 2\text{TBP}$

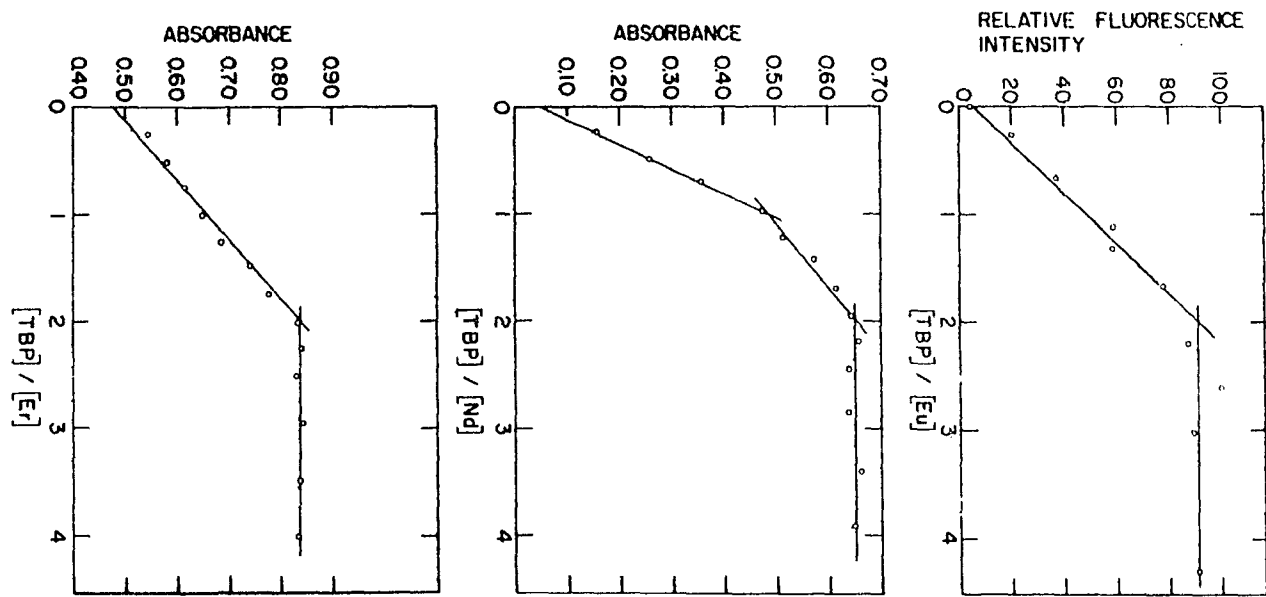


Figure 3.18. Dependence of the absorbance and apparent fluorescence of the organic phase on the molar ratio $[TBP]/[metal]$

was necessary to use only three microliter samples of the organic phase of the extraction mixtures for the fluorescence measurements because the apparent fluorescence intensity was too strong to be measured for larger samples. The extraction data for Nd indicate the formation of a monoadduct which is converted to the diadduct complex at higher concentrations of TBP. These data confirm a stoichiometry of $ML_3 \cdot 2Y$ for the mixed-ligand complexes of the lanthanides with H(FHD) and TBP.

Figure 3.17 shows apparent fluorescence spectra for $Eu(FHD)_3 \cdot 2TBP$ for a sample taken directly from the organic phase of the extraction tube and for $Eu(FHD)_3 \cdot 2TBP$ which was trapped as eluted from the gas chromatograph. The spectra are essentially the same which proves that the complex is being eluted from the gas chromatograph. Similar fluorescence spectra were obtained for samples of $Tb(FHD)_3 \cdot 2TBP$ and $Sm(FHD)_3 \cdot 2TBP$ and these results also indicated that these mixed-ligand complexes are being eluted from the gas chromatograph.

Infrared spectra for H(FHD) and TBPO in CCl_4 are shown in Figure 3.19. The infrared spectrum for TBP is given in Figure 3.8. Assignments for the major infrared spectral bands of H(FHD) and TBP are given in Table 3.6. These assignments agree with those reported in the literature for fluorinated

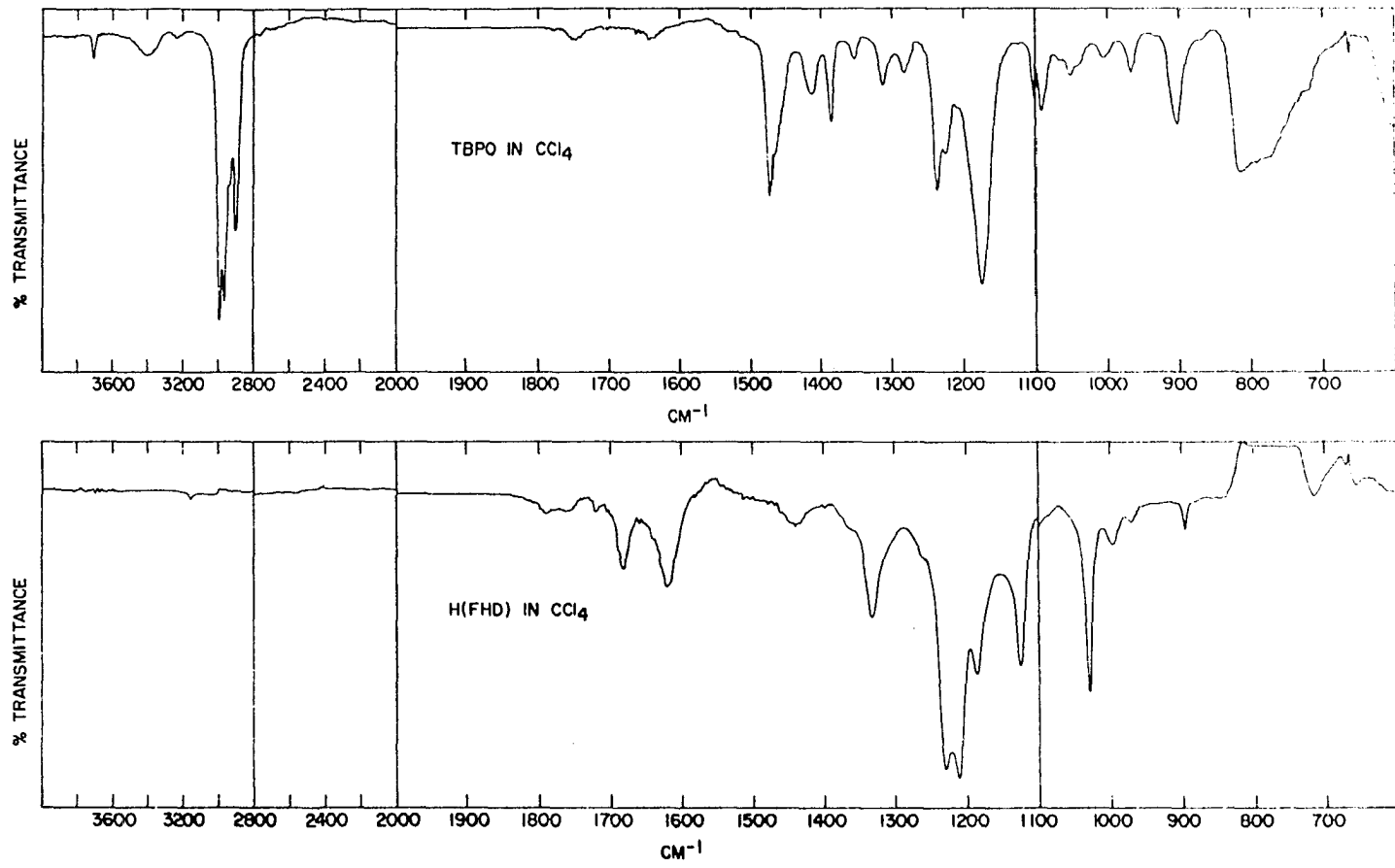


Figure 3.19. Infrared spectra of H(FHD) and TBPO

β -diketones and TBP (10,34,35,36,66,84,87,96,97). The standard curve used to obtain the amount of TBP compared to the amount of H(FHD) in samples collected from the G.C. is shown in Figure 3.20. The standard curve indicates that a ratio of absorbances from 0.6 to 1.1 implies a ratio of neutral donor to ligand in the range 1.5/3 to 2.5/3.

Samples were collected as eluted from the gas chromatograph for selected complexes of the lanthanides and quantitative analysis by infrared spectroscopy was obtained. Table 3.8 lists the results obtained for this study. The absorbance ratios for these complexes all fall in the range 0.6 to 1.1 indicating a stoichiometry of $ML_3 \cdot 2Y$ for the complexes. These data confirm that the mixed-ligand complexes of the lanthanides are eluted from the gas chromatograph with the same stoichiometry as the species which is formed in solvent extraction.

Table 3.8. Ratios of the absorbance of the C-H band at 2990 cm^{-1} to the absorbance of the C-F band at 1127 cm^{-1} for mixed-ligand complexes of H(FHD) and TBP

Complexes	A_{2990}/A_{1127}
Lu	1.00
Er	0.79
Tb	1.06
Eu	0.84
Nd	0.77
La	1.02

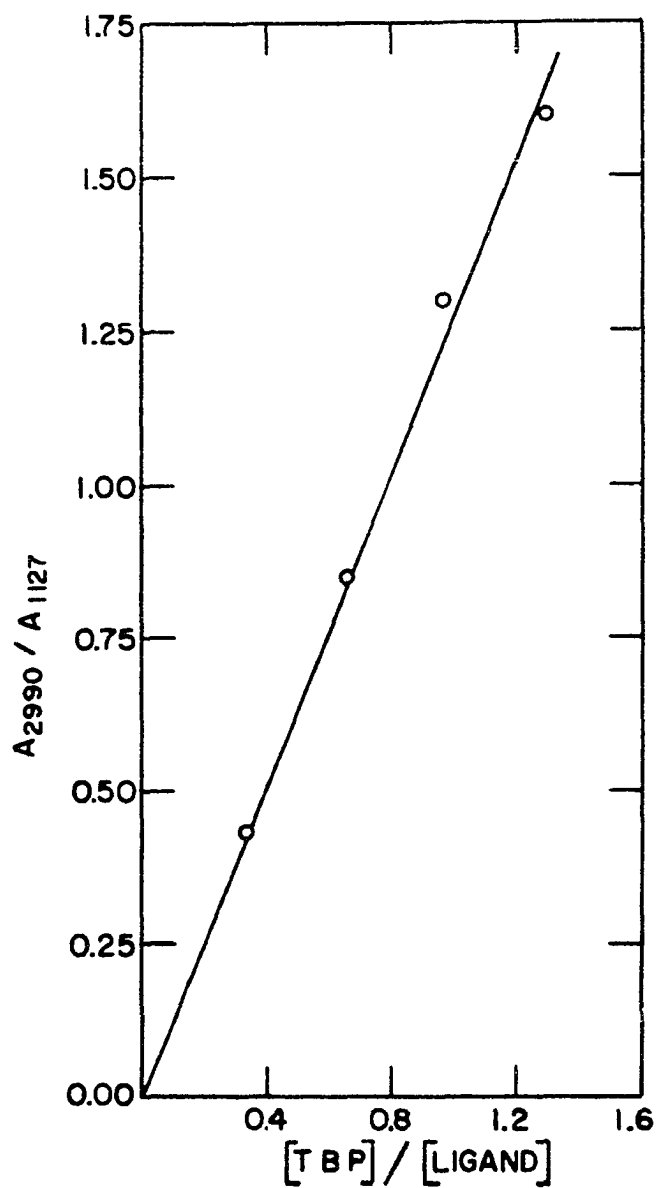


Figure 3.20. Calibration curve relating absorbance ratio to the ratio of TBP to the ligand H(FHD)

Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBP are shown in Figure 3.21. The chromatograms from which these peaks were taken were obtained using a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30. The column temperature was 192°C except for the determination of the complexes of Sm, Nd, Pr, Ce, and La which were determined at a column temperature of 20°C. The chromatographic peaks obtained for these complexes are well defined, symmetric, and exhibit no tailing. A leading edge is visible on the G.C. peaks for Ce and La which is due to slight column overloading. The rather broad peak shown for the Gd complex is caused by the larger sample size used, and not to any difference in the elution behavior.

The mixed-ligand complexes of the lanthanides with H(FHD) and TBP are shown by the data presented above to be thermally stable and volatile at temperatures of about 200°C. The data demonstrate that these complexes can be used to determine the lanthanides by G.C.

b. H(FHD)-DBSO The extraction of selected lanthanides into cyclohexane containing a constant amount of H(FHD) and varying molar ratios of DBSO to metal ion was studied. The molar ratio data shown in Figure 3.22 indicate the forma-

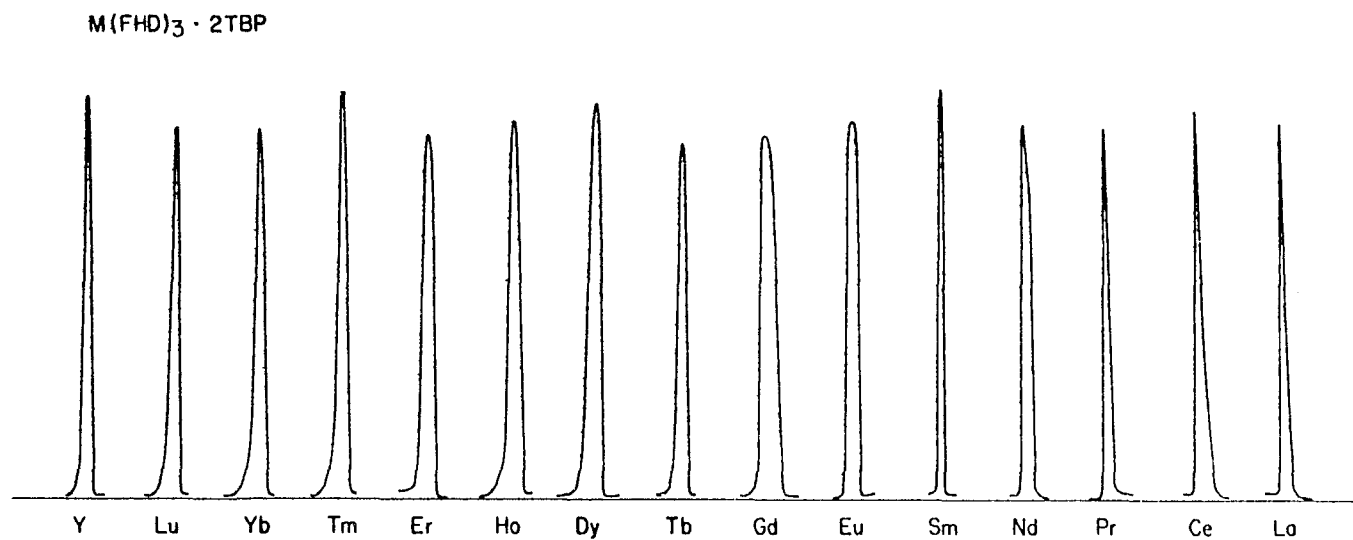


Figure 3.21. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBP

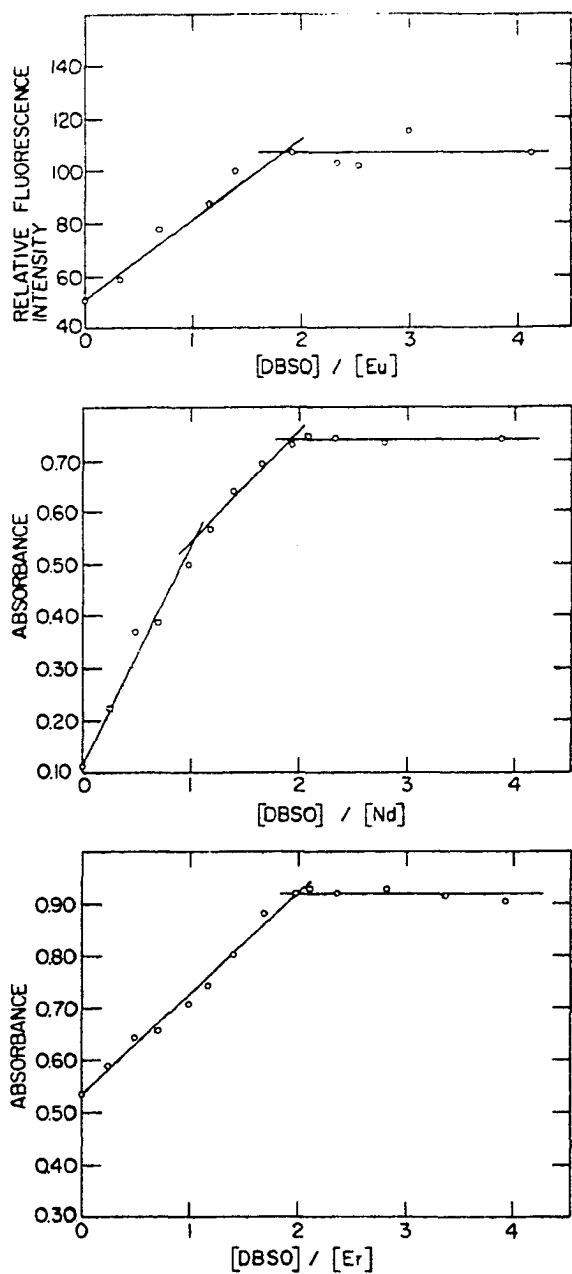


Figure 3.22. Dependence of the absorbance and apparent fluorescence of the organic phase on the molar ratio $[DBSO]/[metal]$

tion of the diadduct complex in the extraction of the lanthanides with H(FHD) and DBSO. The scatter in the data shown for europium is due to the inaccuracy in measurement of very small samples. The extraction data for Nd indicate the formation of a monoadduct complex at low ratios of DBSO to metal ion which is converted to the diadduct complex at higher ratios of DBSO/metal. These data confirm a stoichiometry of $ML_3 \cdot 2Y$ for the extracted mixed-ligand complexes of the lanthanides with H(FHD) and DBSO.

Figure 3.23 shows apparent fluorescence spectra for $Sm(FHD)_3 \cdot 2DBSO$ for a sample taken directly from the organic phase of the extraction tube and for $Sm(FHD)_3 \cdot 2DBSO$ which was trapped as eluted from the gas chromatograph. The spectra are essentially the same, which proves that the complex is being eluted from the chromatograph. Fluorescence spectra were obtained in the same manner for $Tb(FHD)_3 \cdot 2DBSO$ and $Eu(FHD)_3 \cdot 2DBSO$ which confirmed that these complexes are also being eluted from the gas chromatograph.

An infrared spectrum for H(FHD) in CCl_4 is shown in Figure 3.19. An infrared spectrum for DBSO in CCl_4 is shown in Figure 3.8. Assignments for the major infrared spectral bands of H(FHD) and DBSO are given in Table 3.6. These

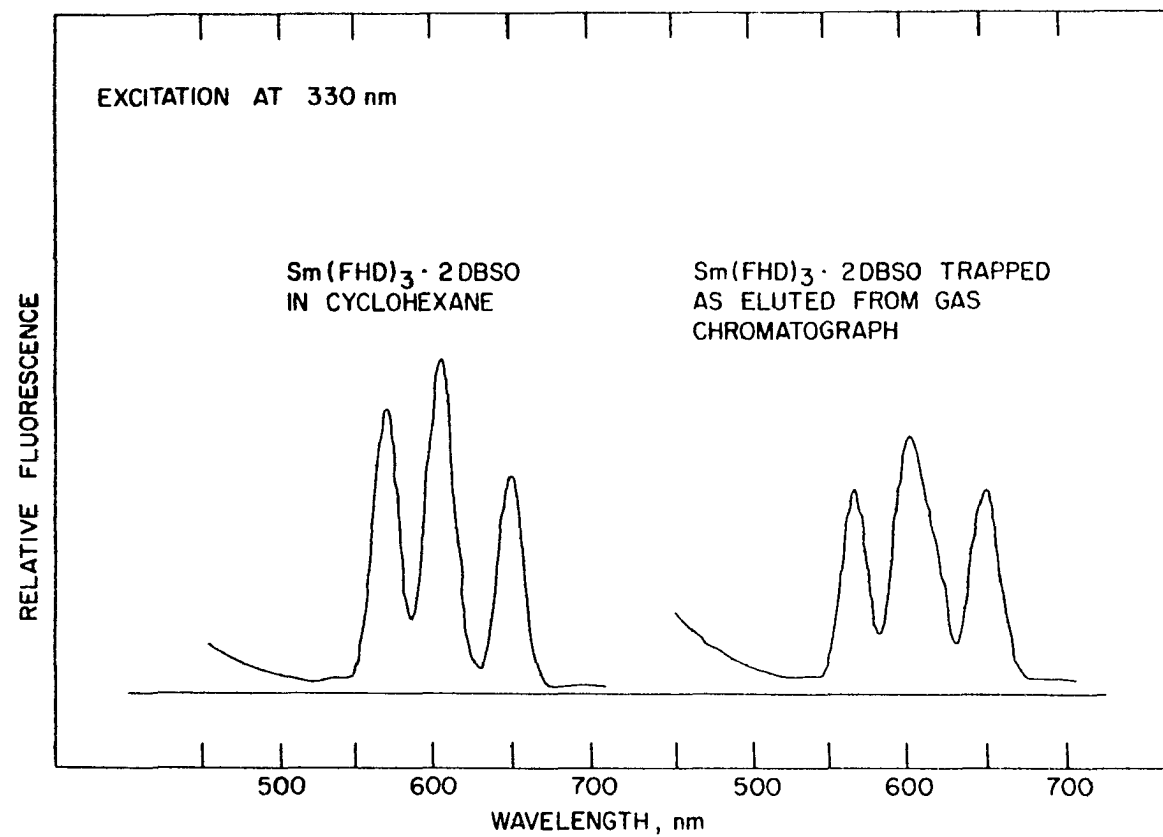


Figure 3.23. Apparent fluorescence spectra for $\text{Sm}(\text{FHD})_3 \cdot 2\text{DBSO}$

assignments agree with those reported in the literature for fluorinated β -diketones and DBSO (10,19,34,36,65,66,84,87,94, 96,97,117). The standard curve used to determine the amount of DBSO relative to the amount of H(FHD) in samples collected from the G.C. is shown in Figure 3.24. The standard curve indicates that a ratio of absorbances from 0.35 to 0.63 implies a ratio of neutral donor to ligand in the range 1.5/3 to 2.5/3.

Selected mixed-ligand complexes of the lanthanides with H(FHD) and DBSO were collected as eluted from the gas chromatograph. Infrared spectra were obtained for these samples and the ratio of DBSO to H(FHD) determined. Table 3.19 shows the results obtained from the quantitative infrared study. The absorbance ratios for these complexes which were collected from the chromatograph all fall in the range 0.35 to 0.63 indicating a stoichiometry of $ML_3 \cdot 2Y$ for the species eluted from the chromatograph.

Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and DBSO are shown in Figure 3.25. The chromatograms from which these peaks were taken were obtained on a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% QF-1. The column temperatures used for the determination of these

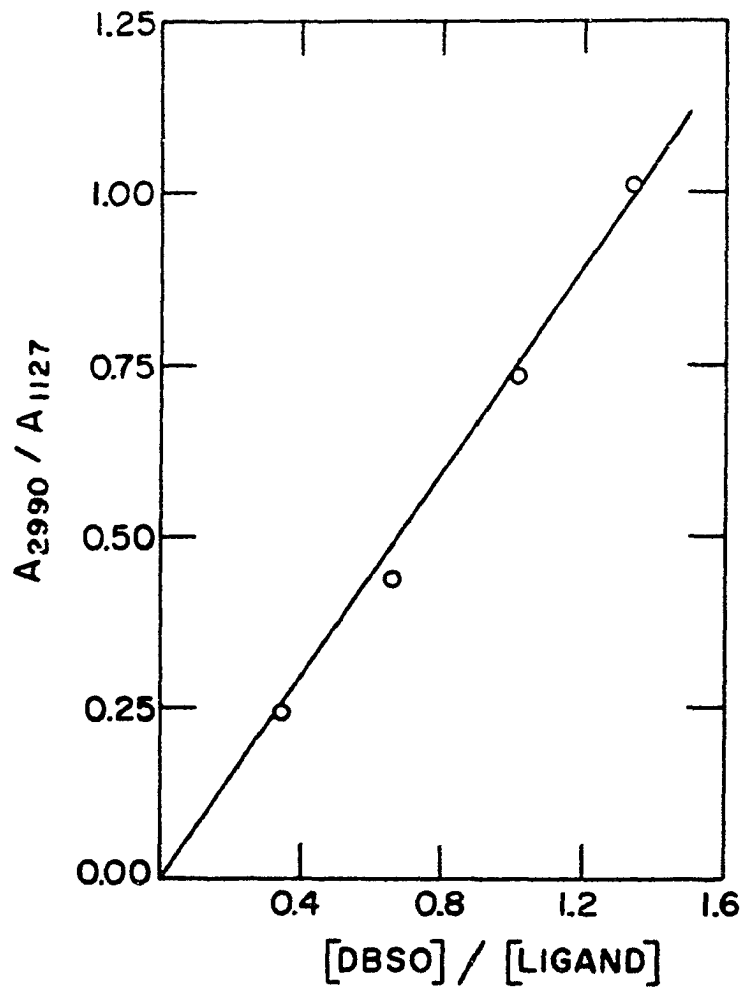


Figure 3.24. Calibration curve relating absorbance ratio to the ratio of DBSO to the ligand H(FHD)

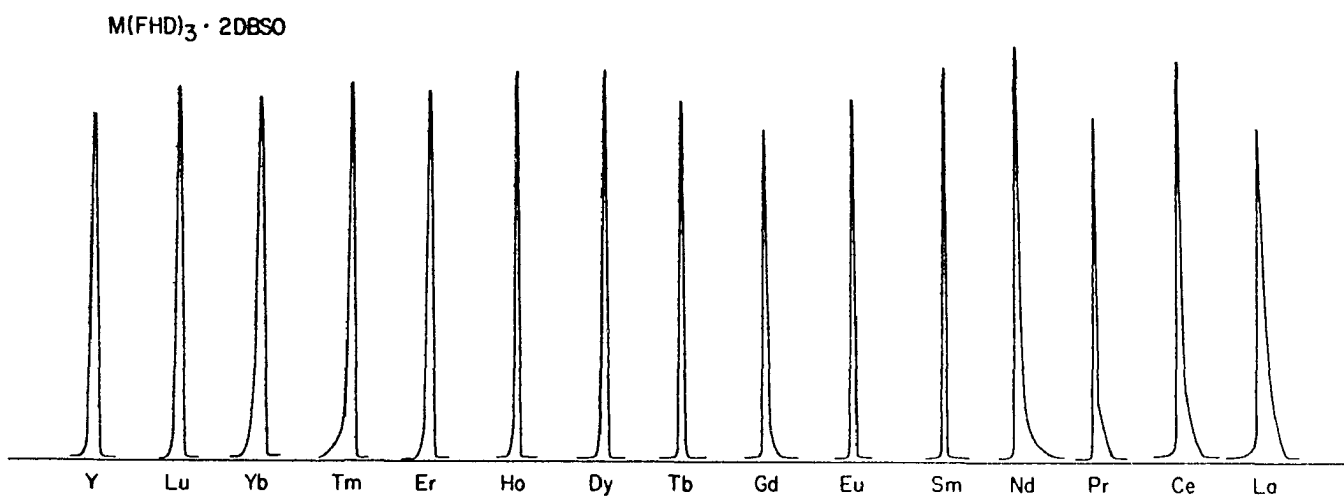


Figure 3.25. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and DBSO

Table 3.9. Ratios of the absorbance of the C-H band at 2990 cm^{-1} to the absorbance of the C-F band at 1127 cm^{-1} for mixed-ligand complexes of H(FHD) and DBSO

Complexes	A_{2990}/A_{1127}
Lu	0.606
Er	0.522
Tb	0.588
Eu	0.598
Nd	0.507
La	0.419

complexes were as follows: 192°C for the complexes of Y, Ho, Dy, Tb, and Gd; 200°C for the complexes of Lu, Yb, Tm, Er, Eu, Sm, and Nd; and 212°C for the complexes of Pr, Ce, and La. The chromatographic peaks obtained for these complexes are sharp, have reasonable widths, and exhibit no tailing. A small leading edge is observed for the chromatographic peaks for the complexes of Nd, Pr, Ce, and La. This leading edge is due to column overloading which will be discussed in Section IV.

The data discussed here for the mixed-ligand complexes of the lanthanides with H(FHD) and DBSO indicate that these complexes are suitable to be used for the determination of the lanthanides by G.C. These complexes are volatile under normal gas chromatographic conditions and elute without decomposition.

c. H(FHD)-TBPO The extraction of selected lanthanides into cyclohexane containing a constant amount of H(FHD) and varying molar ratios of TBPO to metal ion was studied. The molar ratio data shown in Figure 3.26 indicate the formation of the diadduct complex in the extraction of the lanthanides with H(FHD) and TBPO. As before, the scatter in the data for europium is due to inaccurate sampling. For each case studied, these data indicate the formation of a monoadduct complex at low ratios of TBPO to metal ion which is converted to the diadduct complex at higher ratios of TBPO to metal ion. These extraction studies confirm a stoichiometry of $ML_3 \cdot 2Y$ for the extracted mixed-ligand complexes of the lanthanides with H(FHD) and TBPO.

Apparent fluorescence spectra for a sample of $Tb(FHD)_3 \cdot 2TBPO$ taken from the organic phase of an extraction tube and for a sample of $Tb(FHD) \cdot 2TBPO$ collected as eluted from the gas chromatograph are shown in Figure 3.27. These spectra are the same which proves that the complex is being eluted from the chromatograph. Fluorescence spectra for similar pairs of samples were obtained for $Eu(FHD) \cdot 2TBPO$ and $Sm(FHD) \cdot 2TBPO$. These data also confirmed that these complexes are being eluted from the chromatograph.

Infrared spectra for H(FHD) in CCl_4 and TBPO in CCl_4 are

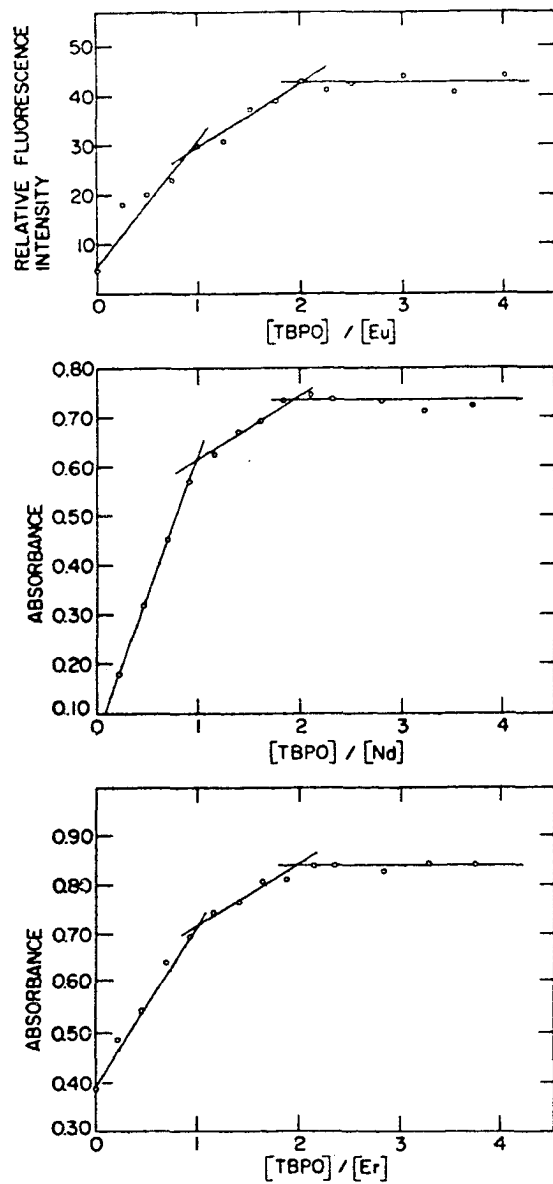


Figure 3.26. Dependence of the absorbance and apparent fluorescence of the organic phase on the molar ratio $[TBPO]/[metal]$

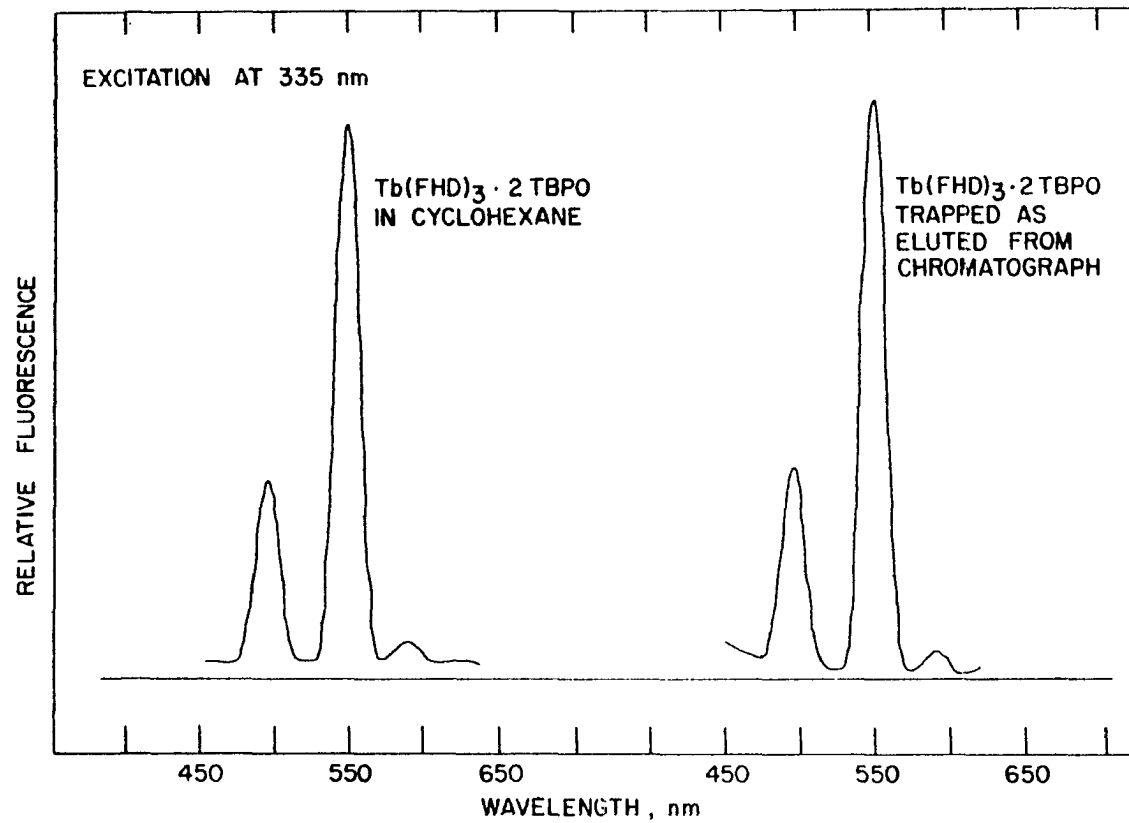


Figure 3.27. Apparent fluorescence spectra for Tb(FHD)₃·2TBPO

shown in Figure 3.19. Assignments for the major infrared spectral bands of H(FHD) and TBPO are given in Table 3.6. These assignments agree with those reported in the literature for fluorinated β -diketones and TBPO (10,34,35,36,66,84,85,96,97,117). The standard curve used to determine the relative amount of TBPO with respect to the amount of H(FHD) in samples collected from the gas chromatograph is shown in Figure 3.28. The standard curve indicates that an absorbance ratio of 0.15 to 0.25 implies a ratio of neutral donor to ligand in the range 1.5/3 to 2.5/3.

Infrared spectra were obtained for samples of several selected complexes of the lanthanides with H(FHD) and TBPO which were collected as eluted from the chromatograph. From these spectra, the relative amount of TBPO with respect to H(FHD) in the samples was determined. Table 3.10 gives the results which were obtained for the quantitative study. The absorbance ratios calculated for these complexes, with the exception of Lu, fall in the range 0.15 to 0.25 indicating a stoichiometry of $ML_3 \cdot 2Y$ for the species eluted from the chromatograph. The absorbance ratio for the Lu complex indicates a slight deficiency of TBPO in the complex as eluted from the gas chromatograph compared to the species extracted. It is possible that the Lu complex loses some TBPO during

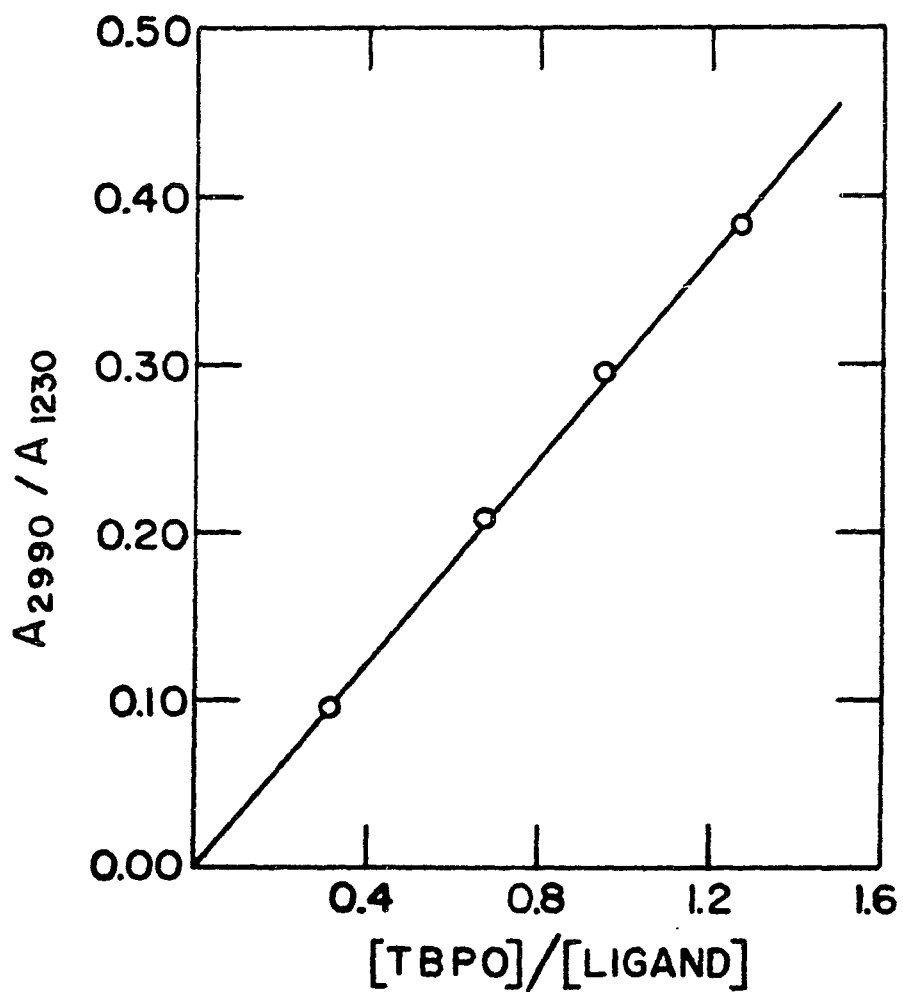


Figure 3.28. Calibration curve relating absorbance ratio to the ratio of TBPO to the ligand H(FHD)

Table 3.10. Ratios of the absorbance of the C-H band at 2990 cm^{-1} to the absorbance of the C-F band at 1230 cm^{-1} for mixed-ligand complexes of H(FHD) and TBPO

Complexes	A_{2990}/A_{1230}
Lu	0.132
Er	0.182
Tb	0.188
Eu	0.189
Nd	0.178
La	0.188

analysis by G.C. Shigematsu *et al.* (115) have shown that the stability of the second adduct for mixed-ligand complexes of this type decreases from La to Eu to Lu. This decrease in stability could account for the loss of some TBPO from the complex of Lu during analysis by G.C. which places the complex under thermal stress. No other indication of decomposition of the mixed-ligand complex of Lu with H(FHD) and TBPO was observed in this study.

Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBPO are shown in Figure 3.29. The chromatograms from which these peaks were taken were obtained on a 4' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 5% SE30. The column temperature for the determination of these complexes

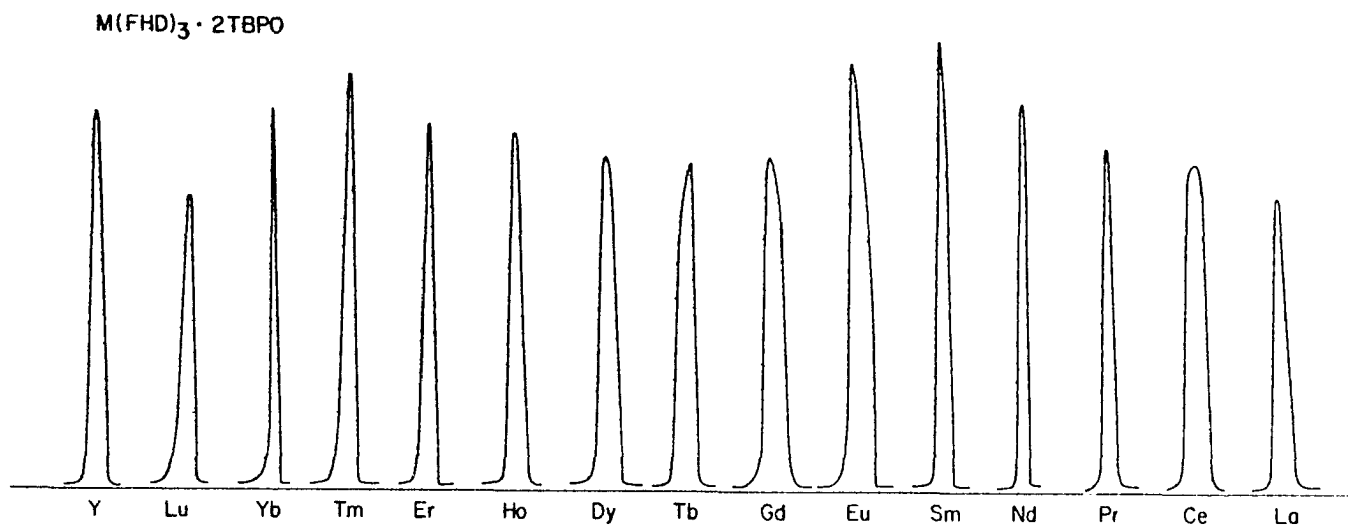


Figure 3.29. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBPO

was 202°C except for the complex of Sm which was determined at 212°C and the complexes of Nd, Pr, Ce, and La which were determined at a column temperature of 220°C. The chromatographic peaks for these complexes are symmetric and exhibit no tailing. It was difficult to obtain undistorted peaks for these complexes because the column was very easily overloaded. However, there was no evidence of decomposition of the complexes.

The data acquired concerning the mixed-ligand complexes of the lanthanides with H(FHD) and TBPO indicate that these complexes are stable and volatile under normal gas chromatographic conditions. Small sample sizes were needed to prevent column overloading during determination of these complexes, but satisfactory elution patterns could be obtained. These data indicate that these complexes can be used for the determination of the lanthanides by G.C.

8. Solvent extraction and determination by G.C. of mixed-ligand complexes of UO_2^{+2} and Th(IV)

Several mixed-ligand complexes of UO_2^{+2} and Th(IV) were evaluated to ascertain if it were feasible to determine these complexes by G.C. Table 3.11 indicates the complexes which were considered. Solid complexes were isolated for some of the mixed-ligand complexes of UO_2^{+2} and Th(IV). Analytical

data for these are shown in Table 3.12. These data indicate that the stoichiometry for the mixed-ligand complexes is $\text{Th(L)}_4 \cdot \text{Y}$ and $\text{UO}_2(\text{L})_2 \cdot \text{Y}$ where $\text{L} = \beta$ -diketone and $\text{Y} =$ neutral donor. It is of course possible that other species exist in solution. However, work with similar mixed-ligand systems has indicated the same stoichiometry under solvent extraction conditions for mixed-ligand complexes of UO_2^{+2} and Th(IV) (49,50,53,120,148).

Table 3.11. Mixed-ligand complexes used in the gas chromatographic study

UO_2^{+2}	Th(IV)
$(\text{HFA})_2 \cdot \text{TBPO}$	$(\text{HFA})_4 \cdot \text{TBPO}$
$(\text{DODEFOD})_2 \cdot \text{TBP}$	$(\text{DODEFOD})_4 \cdot \text{TBP}$
$(\text{DODEFOD})_2 \cdot \text{DBSO}$	$(\text{DODEFOD})_4 \cdot \text{DBSO}$
$(\text{DODEFOD})_2 \cdot \text{TBPO}$	$(\text{DODEFOD})_4 \cdot \text{TBPO}$
$(\text{FHD})_2 \cdot \text{TBP}$	$(\text{FHD})_4 \cdot \text{TBP}$
$(\text{HFA})_2 \cdot \text{TBP}$	$(\text{HFA})_4 \cdot \text{TBP}$
$(\text{FHD})_2 \cdot \text{DBSO}$	$(\text{FHD})_4 \cdot \text{DBSO}$
$(\text{HFA})_2 \cdot \text{DBSO}$	$(\text{HFA})_4 \cdot \text{DBSO}$
$(\text{FHD})_2 \cdot \text{TBPO}$	$(\text{FHD})_4 \cdot \text{TBPO}$

Table 3.12. Analytical results for UO_2^{+2} and Th(IV) complexes

Compound	M.P. °C	% Metal		% Carbon		% Hydrogen	
		Calcd	Found	Calcd	Found	Calcd	Found
$\text{UO}_2(\text{HFA})_2 \cdot \text{DBSO}$	82	31.83	31.45	25.48	25.27	2.62	2.60
$\text{UO}_2(\text{FHD})_2 \cdot \text{DBSO}$	58	25.75	26.51	25.20	25.05	2.12	2.14
$\text{Th}(\text{HFA})_4 \cdot \text{DBSO}$	82	18.92	19.11	26.58	26.68	1.61	1.89
$\text{Th}(\text{TFA})_4 \text{DBSO}$	oil	22.95	22.53	33.27	33.51	3.79	4.29

a. Determination by G.C. of mixed-ligand complexes of UO_2^{+2} and Th(IV) Table 3.13 lists the GLC columns which were used for the study of complexes of UO_2^{+2} and Th(IV). Figure 3.30 shows chromatograms for the determination of $\text{UO}_2(\text{FHD})_2 \cdot \text{TBP}$ and $\text{Th}(\text{FHD})_4 \cdot \text{TBP}$. Attempts to resolve these complexes in a determination of a mixture of the complexes by G.C. were not successful. Satisfactory chromatographic peaks were not obtained for the HFA-TBP complexes with UO_2^{+2} and Th(IV).

Table 3.13. GLC columns used for the determination of mixed-ligand complexes of UO_2^{+2} and Th(IV)

Column	Size and Type	Packing
A	16" x 1/4" stainless steel	10% SE30 on Chromosorb W
B	16" x 1/4" stainless steel	20% QF-1 on Chromosorb W
C	6' x 1/8" stainless steel	4% SE30 on Chromosorb W
D	4' x 1/4" glass	5% SE30 on Chromosorb W

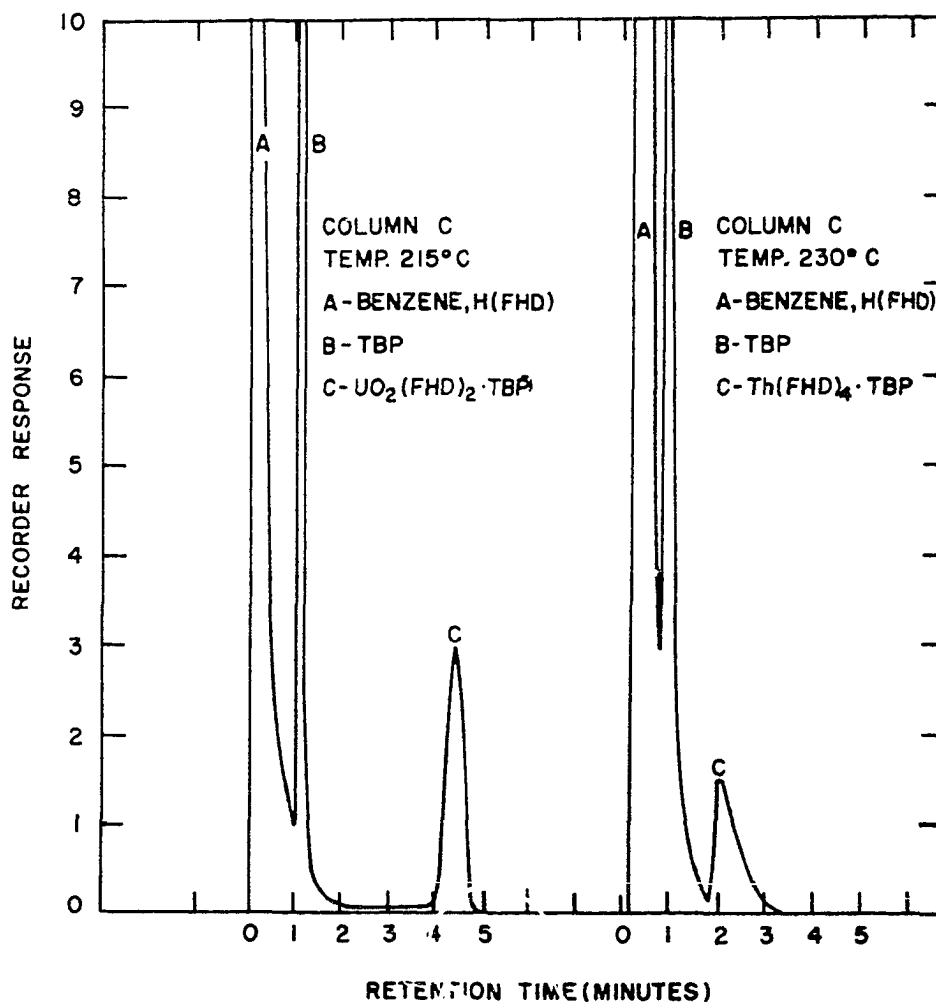


Figure 3.30. Gas chromatograms for mixed-ligand complexes of UO_2^{+2} and $\text{Th}(\text{IV})$ with $\text{H}(\text{FHD})$ and TBP

Figure 3.31 shows a composite chromatogram for determinations of $\text{UO}_2(\text{HFA})_2 \cdot \text{TBPO}$ and $\text{UO}_2(\text{FHD})_2 \cdot \text{TBPO}$. Multiple peaks are observed in both these determinations. These data indicate that these mixed-ligand complexes are not stable enough for determination by G.C. An identifiable peak for the HFA-TBPO complex of Th(IV) was not observed, however a relatively good chromatogram was obtained for $\text{Th}(\text{FHD})_4 \cdot \text{TBPO}$.

The results obtained for the study of mixed-ligand complexes of UO_2^{+2} and Th(IV) using the β -diketone H(DODEFOD) were inconclusive. Column D was used for the study of the DODEFOD complexes. Poor chromatograms were obtained for the complexes using H(DODEFOD), but it may be that this was due to the use of insufficient sample size to obtain a response on the flame ionization detector. It was found that larger samples were needed to obtain a reasonable response for mixed-ligand complexes of UO_2^{+2} and Th(IV) than for the complexes of the lanthanides. This information was discovered after most of the complexes of UO_2^{+2} and Th(IV) with H(DODEFOD) had been evaluated and at a time when the ligand was not available for further work. It is probable that results could be obtained for H(DODEFOD) complexes with UO_2^{+2} and Th(IV) which would be very similar to those reported for the complexes with

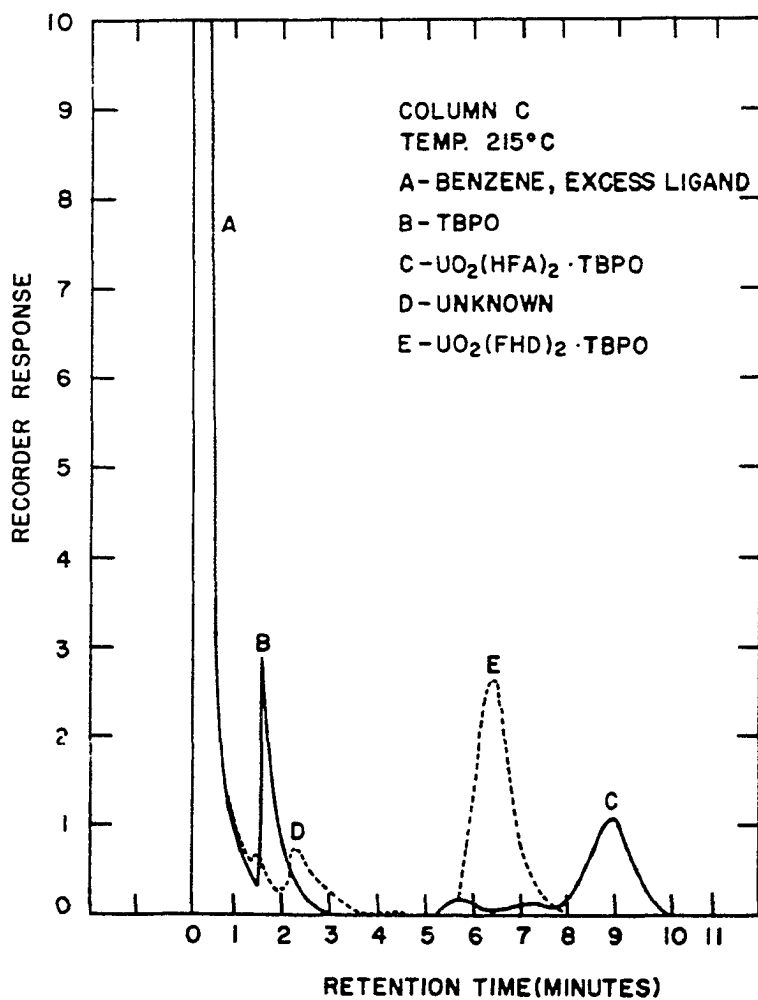


Figure 3.31. Gas chromatograms for mixed-ligand complexes of UO_2^{+2} with H(HFA) and TBPO and with H(FHD) and TBPO

H(FHD).

Figure 3.32 shows a chromatogram for a single injection of a mixture of $\text{Th}(\text{FHD})_2 \cdot \text{DBSO}$ and $\text{UO}_2(\text{FHD})_2 \cdot \text{DBSO}$. Attempts to completely resolve this mixture were not successful. Single injections of the individual complexes gave excellent results. These data indicate that the mixed-ligand complexes of UO_2^{+2} and Th(IV) with H(FHD) and DBSO can be determined by G.C.

b. Quantitative determination of mixed-ligand complexes of UO_2^{+2} and Th(IV) with H(HFA) and DBSO The chromatogram for a mixture of $\text{UO}_2(\text{HFA})_2 \cdot \text{DBSO}$ and $\text{Th}(\text{HFA})_4 \cdot \text{DBSO}$ is shown in Figure 3.33. This chromatogram illustrates the excellent separation of the complexes of UO_2^{+2} and Th(IV). The column temperature for this analysis was held at 192°C until the Th(IV) complex was eluted, then the temperature was elevated to 210°C for elution of the UO_2^{+2} complex. The small rise in baseline after the temperature elevation which is indicated at point D in Figure 3.33, is probably due to the effect of thermal changes occurring from the step program. As can be seen, it does not interfere with the analysis. Baseline separation for the HFA-DBSO complexes was also achieved on column A, but not with as much resolution as was observed on Column B.

The mixed-ligand complexes $\text{UO}_2(\text{HFA})_2 \cdot \text{DBSO}$ and $\text{Th}(\text{HFA})_4 \cdot$

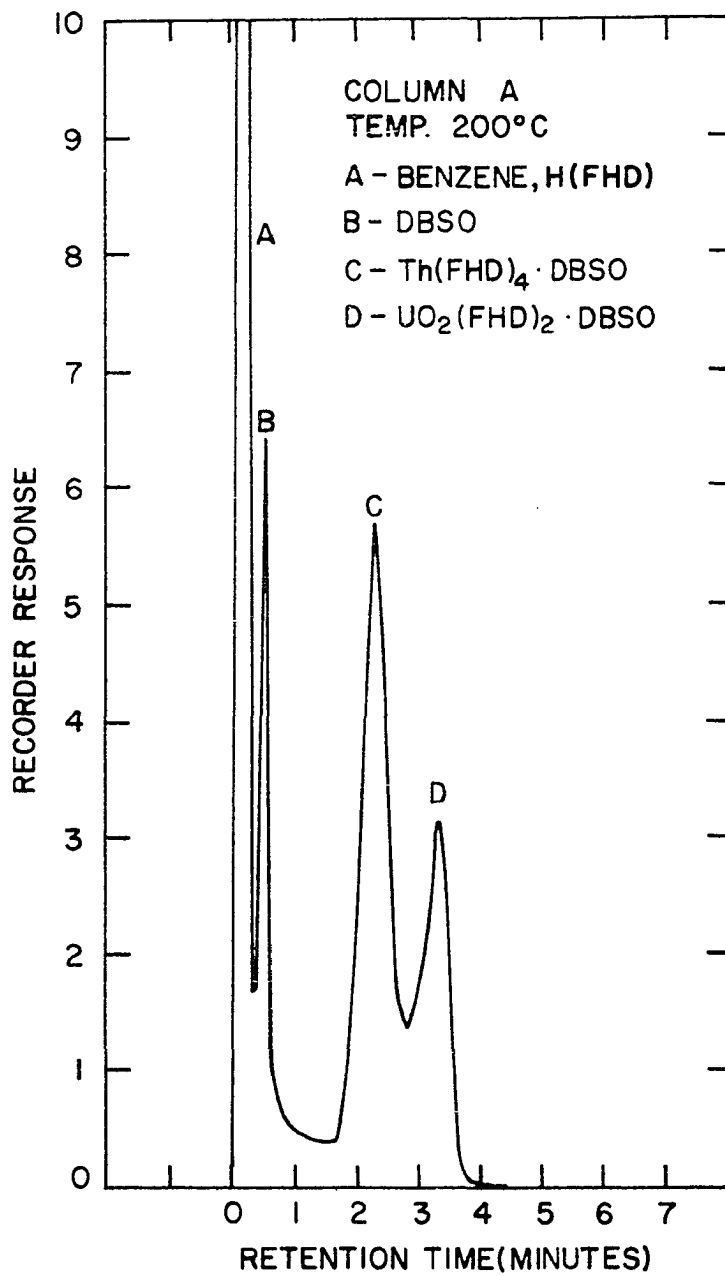


Figure 3.32. Gas chromatogram for mixed-ligand complexes of UO_2^{+2} and Th(IV) with H(FHD) and DBSO

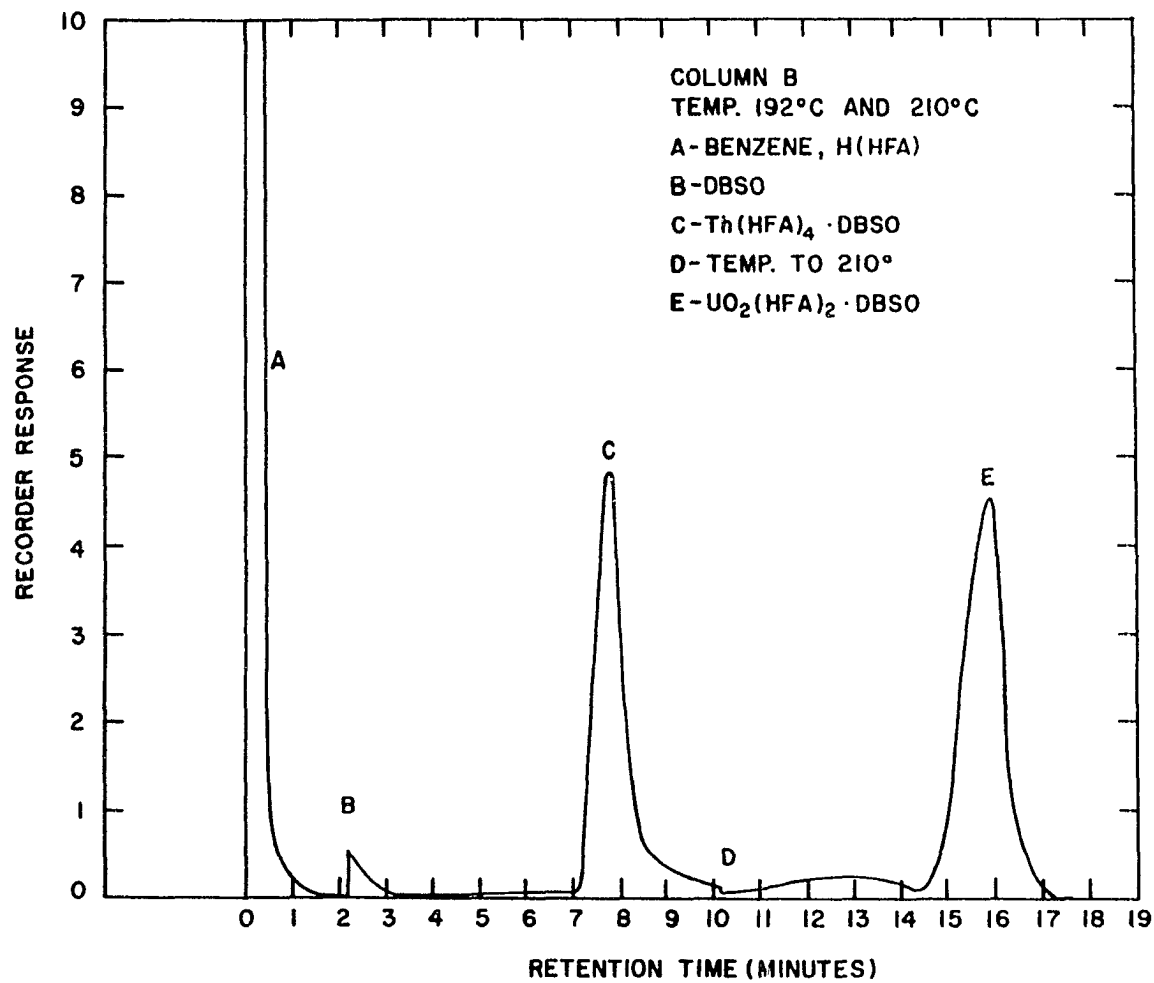


Figure 3.33. Gas chromatogram for mixed-ligand complexes of UO_2^{+2} and Th(IV) with H(HFA) and DBSO

DBSO were individually trapped as eluted from the chromatograph. Data for the carbon-hydrogen analysis of these trapped complexes are shown in Table 3.14.

Table 3.14. Carbon and hydrogen results on complexes trapped from the gas chromatograph

	Carbon		Hydrogen	
	Calcd	Found	Calcd	Found
$\text{UO}_2(\text{HFA})_2 \cdot \text{DBSO}$	25.48	24.59	2.62	2.36
$\text{Th}(\text{HFA})_4 \cdot \text{DBSO}$	27.42	27.64	2.13	2.49

These data indicate that complexes of the stoichiometry noted in the table are being eluted from the chromatograph.

During the analysis by G.C. of $\text{Th}(\text{HFA})_4 \cdot \text{DBSO}$ which had been dissolved into benzene from a solid complex preparation, a chromatographic peak was observed at the retention time of DBSO. It is known that very little excess DBSO existed in the solid complex, and therefore it appears that some DBSO is flashed away from the thorium complex in the inlet. However, examination of the inlet after analysis of the thorium complex revealed no residue, and the carbon-hydrogen data shown in Table 3.14 indicate that the thorium complex is being eluted substantially intact.

Standard solutions of $\text{Th}(\text{HFA})_4 \cdot \text{DBSO}$ and $\text{UO}_2(\text{HFA})_2 \cdot \text{DBSO}$ were made in the range 1 mg metal/ml to 120 mg metal/ml.

Solutions in the range 1 mg metal/ml to 10 mg metal/ml were prepared by solvent extraction, while solutions of higher concentration were prepared by weighing out the solid complex followed by dissolution in known volumes of benzene.

Twenty-microliter samples of the solution of the complexes in benzene were injected into the gas chromatograph. Two or three injections were made to equilibrate the column to each particular sample, then three to five samples were run and the average area under the chromatographic peak of the complex was determined by the Disc Integrator.

Figure 3.34 shows calibration curves for the complexes of Th(IV) and UO_2^{+2} . Calibration curves were drawn plotting integrator counts versus g metal $\times 10^{-3}$ /ml. The calibration curves were checked periodically over a period of two weeks and did not vary significantly. Samples in the 5 mg metal/ml and 10 gm metal/ml range were chromatographed using solutions obtained from both solvent extraction and dissolution of the solid complex. The calibration points were identical for samples prepared by these different methods. Furthermore, the calibration curve did not vary when different gas chromatographic columns were used.

It should be noted that the response for a given weight of thorium as shown in Figure 3.33 is greater than that for

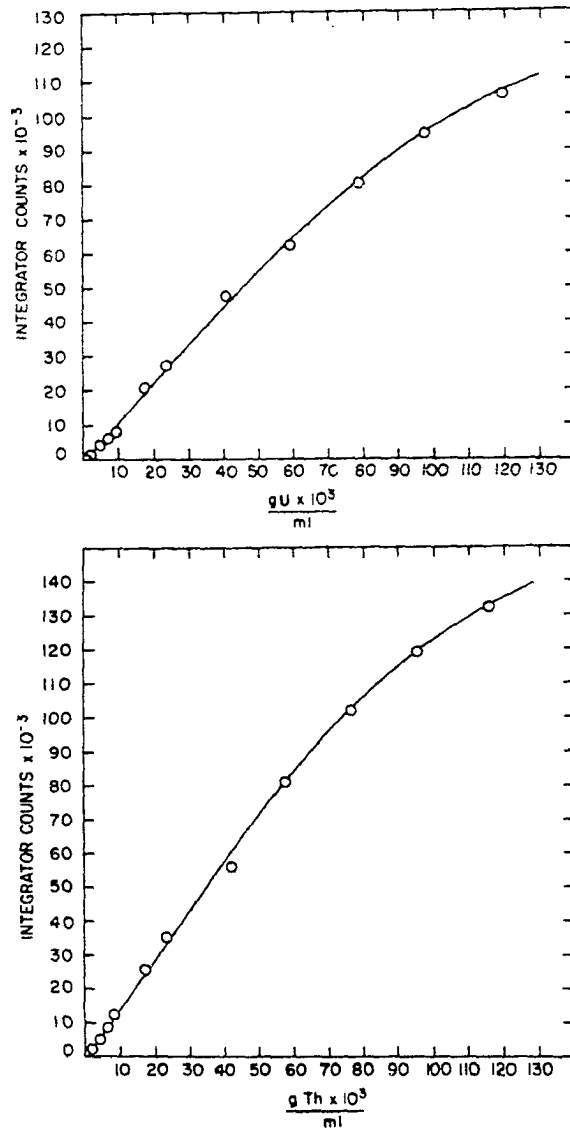


Figure 3.34. Calibration curves of concentration range 1×10^{-3} g metal/ml to 120×10^{-3} g metal/ml

an equivalent weight of uranium. This is to be expected since the molecular weight of $\text{Th}(\text{HFA})_4 \cdot \text{DBSO}$ is 1225.9 g/mole while that of $\text{UO}_2(\text{HFA})_2 \cdot \text{DBSO}$ is only 848.1 g/mole. Assuming the thermal conductivity of the mixed-ligand species to be approximately the same, the thermal conductivity detector should respond more to the heavier complex.

Detection limits were determined for both mixed-ligand complexes used in the quantitative study. The detection limit was taken to be that minimum amount of mixed-ligand complex necessary to give a chromatographic peak response for the complex equal to or greater than twice the background response. Detection limits were observed as follows:

Th: 0.4×10^{-3} g/ml, and U: 0.6×10^{-3} g/ml.

Four unknown samples were prepared by an independent worker and analyzed by G.C. The data obtained for the analysis of the unknowns are shown in Table 3.15.

There should be no major interferences for this method of analysis of UO_2^{+2} and Th(IV). Mitchell (77) has shown that various mixed-ligand complex systems can be utilized to isolate UO_2^{+2} and Th(IV) from common interference such as Sc(III), Fe(III), Al(III), and the lanthanides. After isolation by extraction, the UO_2^{+2} and Th(IV) can easily be prepared as the HFA-DBSO complexes for analysis by G.C.

Table 3.15. Analysis of unknowns

	U			Th		
	Present	g x 10 ⁻³ /ml Found	% Error	Present	g x 10 ⁻³ /ml Found	% Error
1. ^a	4.9	4.9	0.0	4.4	4.7	5.8
2. ^b	36.4	34.3	5.8			
3. ^a				23.7	24.4	3.0
4. ^b	20.8	19.3	7.2	14.1	13.4	5.0

^aPrepared by solvent extraction.

^bPrepared by weighing out solid complex.

IV. AN INVESTIGATION OF GAS CHROMATOGRAPHIC COLUMNS USED IN DETERMINATION OF MIXED-LIGAND COMPLEXES

A. Introduction

This work will entail a study of the gas chromatographic columns which are useful in the determination of mixed-ligand complexes by G.C. A survey of different types of packed columns was made to ascertain the kind of solid support, the type of liquid loading and the amount of liquid loading which are best suited to the determination of mixed-ligand complexes. The study will report specific liquid phases in which mixed-ligand complexes will partition. Data are presented to illustrate the nature of the partitioning process between lanthanide complexes and selected liquid phases.

Uden and Jenkins (138) have reported unusual adsorption and displacement effects in the G.C. of metal chelates. Similar phenomena have been observed during the determination of mixed-ligand complexes by G.C., and will be reported in the following discussion. In addition, the relationship between the chemical composition of mixed-ligand complexes, and the retention of mixed-ligand complexes by the gas chromatographic column has been evaluated. Data are presented which illustrate the effect of chemical composition on the retention of

mixed-ligand complexes.

B. Experimental

1. Apparatus

a. Gas chromatograph A Beckman GC-4 gas chromatograph was used for the column studies. The chromatograms were recorded with a Bristol model 560 Dynamaster recorder equipped with a Disc Integrator.

b. Thermogravimetric analyzer A DuPont Model 950 thermogravimetric analyzer was used to obtain all thermograms.

c. Fluorimeter Fluorescence data were taken on an Aminco-Bowman Spectrophotofluorimeter equipped with a Moseley X-Y recorder.

2. Reagents and materials

a. Solid supports Solid support materials were obtained from Applied Science Laboratories or Analabs, Inc.

b. Liquid phases Commercial liquid phases were obtained from Applied Science Laboratories or Analabs, Inc. Organic alkyl phosphates and alkyl phosphine oxides were obtained from laboratory stock.

c. Columns Pyrex, borosilicate glass tubing was used for the glass columns and was obtained from laboratory stock. Stainless steel columns were prepared from laboratory stock

stainless steel tubing.

d. Solvents All solvents were reagent grade.

3. Techniques

a. Preparation of column packing An adaptation of the method described by Butts (14) was used to prepare column packings. Five to ten grams of dry solid support is placed on the glass frit in a 2" x 10" cylindrical tube. A solution of the stationary phase, twice the wetting volume of the support, is poured into the tube and mixed with the support. The excess solution is drained from the support through a stopcock below the glass frit. Then filtered air is passed up through the packing while heat is applied with infrared heat lamps. In this manner the solvent is removed leaving a uniform coating of liquid phase on the solid support.

b. Packing and conditioning of columns Both glass and stainless steel columns were rinsed with acetone and ethanol and air dried before packing. Dry column packing was poured into the chromatographic columns and compacted with the aid of a Burgess Vibro-graver. The ends of the columns were plugged with glass wool.

Columns were conditioned at about 25°C to 50°C below the indicated temperature maxima for the particular liquid phase. All columns were condition from 4 to 6 hours at the appropri-

ate temperature with a moderate helium flow, 30 to 40 ml/min.

c. Sample collection Samples were collected from the gas chromatograph in glass collection traps. Details of the technique were discussed in Section III.

4. Analytical determinations

a. Determination of non-silicone liquid phases The weight per cent of liquid coating for non-silicone liquid phases was determined by weight difference. A one gram sample of column packing was weighed into a crucible. The sample was then fired in a muffle furnace at 900°C for one hour to burn off the liquid phase from the solid support.

The percentage of liquid coating was calculated as follows:

% liquid coating =

$$\frac{\text{g column packing} - \text{g solid support after firing} \times 100}{\text{g solid support after firing}}$$

b. Determination of silicone liquid phases The weight per cent of liquid coating for silicone liquid phases cannot be determined by burning off the liquid, because these phases leave a SiO₂ residue upon burning. The amount of silicone liquid phase on column packings was determined by washing a known amount of packing in a filter funnel with copious amounts of the solvent used to dissolve the liquid phase. The percentage silicone liquid coating was calculated as follows:

% liquid coating =

$$\frac{\text{g column packing} - \text{g solid support after washing} \times 100}{\text{g solid support after washing}}$$

c. Identification of eluted species Complexes of samarium, europium and terbium were identified by comparing the apparent fluorescence of samples eluted from the gas chromatograph to that of the organic phase of extraction mixtures.

C. Results and Discussion

1. Evaluation of gas chromatographic columns for the determination of metal complexes

a. Lightly loaded gas chromatographic columns Early work on the determination of metal chelated by G.C. utilized lightly loaded columns (83). Lightly loaded gas chromatographic columns employ glass beads as the solid support and use one per cent or less liquid phase. These lightly loaded columns have been found useful for the determination of species with low volatility because the small amount of liquid phase and the glass bead solid support do not highly retain species (38). There is very little gas-solid interaction with glass bead solid supports which have been silanized, and the amount of gas-liquid partitioning will be small due to the small total amount of liquid phase in the column.

Table 4.1 lists the lightly loaded gas chromatographic columns evaluated in this study. Columns number 1, 2, and 3 employed mixed liquid phases. These were prepared for the determination of chelates of the lanthanides with H(FOD). It was of interest to see if any interaction could be observed between an organic base used as a liquid phase and the $M(\text{FOD})_3$ chelates where M = lanthanide ion. Since $M(\text{FOD})_3$ chelates have at least two coordination sites partially available for interaction, it was hoped that some resolution of these species could be obtained as a result of the interaction of the chelates with the organic base on the column. Chromatograms for $\text{Er}(\text{FOD})_3$, $\text{Tb}(\text{FOD})_3$, and $\text{Pr}(\text{FOD})_3$ were obtained on columns 1, 2, 3, 13, 14, and 15. The chromatograms did not indicate significant resolution of these chelates with the exception of column 15 which absorbed the chelates. Columns 1, 2, 3, 13 and 14 gave results very similar to column 4. These data indicate that the organic bases interact with the complexes much as does the hydrocarbon liquid phase Apiezon L. Perhaps the basic functional groups of these materials are oriented toward active sites on the column support and are not available for interaction with the solute as it passes through the column so that a hydrocarbon type liquid phase is present in both cases.

Table 4.1. Lightly loaded gas chromatographic columns used for determination of metal complexes

1.	0.7% Apiezon L plus 0.2% TOPO	9.	0.5% SE30
2.	0.7% Apiezon L plus 0.2% TPPO	10.	0.2% SE30
3.	0.7% Apiezon L plus 0.2% MHDPO	11.	0.1% SE30
4.	0.5% Apiezon L	12.	0.1% QF-1
5.	0.5% ZE7	13.	0.5% TOPO
6.	0.2% ZE7	14.	0.5% TPPO
7.	0.1% ZE7	15.	0.5% MHDPO
8.	0.7% SE30		

It was not possible to elute the $M(\text{FOD})_3$ chelates from column 15 which used MHDPO as a liquid phase, at temperatures up to 250°C . Above this temperature the MHDPO began to bleed from the column. These data indicate that these chelates will interact with organic bases on a chromatographic column. However, it may be very difficult to find liquid phases which will interact with the chelates without retarding them so much that determination by G.C. is impossible.

Mixed-ligand complexes of selected lanthanides with $\text{H}(\text{DODEFOD})$ and TBP were determined on columns 5, 6, 7, 8, 9, 10, 11, 12. It was possible to elute mixed-ligand complexes from these lightly-loaded columns at relatively low temperatures. For example, $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ was eluted from column 11 which employed SE30 for a liquid phase in 3.5 min. at a temperature of 170°C . However, in general the resolution obtained on the lightly loaded columns was poor. In particu-

lar, it was difficult to completely resolve the mixed-ligand complexes from the excess neutral donor which was present in the extraction mixtures. An acceptable determination of mixed-ligand complexes of the lanthanides by G.C. requires the complete resolution of the complex from the excess reagents in the extraction mixture. The data obtained in this study indicate, therefore, that lightly loaded columns are not adequate for the determination of mixed-ligand complexes.

b. Aliphatic hydrocarbon and polar liquid phases

The most commonly used liquid phases of the hydrocarbon type are the Apiezon series of high molecular weight aliphatic hydrocarbons (32). Column packings were prepared using Chromosorb W as the solid support and Apiezon L as the liquid phase with liquid phase loadings of about 1, 5, 10, 20 per cent by weight. These columns utilizing Apiezon L as the liquid phase were found to be unsatisfactory for the determination of mixed-ligand complexes of the lanthanides. Temperatures of 220° to 230°C were needed to elute FHD-TBP complexes in less than 5 min and peak widths were 1 to 2 min wide even at these temperatures. Of more importance was the fact that the columns using Apiezon L did not resolve the mixed-ligand complex from the excess TBP in the extraction mixture. On a 4' x 1/4"-glass column packed with Chromosorb W coated

with 10% Apiezon L, the retention time for both $\text{Eu}(\text{DODEFOD}) \cdot 2\text{TBP}$ and TBP was 3.8 min at 215°C . These data indicate that the hydrocarbon type liquid phases do not perform adequately in the determination of mixed-ligand complexes.

Three polar liquid phases were studied, Lexan and Ethylene Glycol Adipate which are polyesters and Versamide 900 which is a polyamide. Column packings were prepared using Chromosorb W as the solid support and about 5% liquid loading of each of these polar liquid phases. Glass columns (4' x 1/4") were packed with each of these column packings. The elution of $\text{Er}(\text{DODEFOD}) \cdot 2\text{TBP}$ was studied on each of the columns and it was found that this mixed-ligand complex could not be eluted from any of the columns at temperatures up to 230°C : These data indicate that polar liquid phases either absorb or very severely retard mixed-ligand complexes. Hence, these liquid phases cannot be used for the determination of mixed-ligand complexes.

c. Porous polymers and fluorine-containing liquid phases

Two porous polymers were studied, Porapak Q and Porapak T. Porapak is the trade name of Waters Associates for a series of porous polymers composed of ethylvinylbenzene cross-linked with divinylbenzene to form a uniform structure of a

distinct pore size. The polymers are modified by copolymerization with different polar monomers to produce beads of varying polarity. Type Q is a non-polar polymer while type T is moderately polar. A 4' x 1/4"-glass column was packed for each of these two polymers and an attempt was made to determine $\text{Er}(\text{DODEFOD}) \cdot 2\text{TBP}$ on each column. A chromatographic peak for the complex was not observed. After several attempts to determine the erbium complex, a discoloration could be observed at the top of the column on the inlet side. These data indicate that the mixed-ligand complex is either absorbed by the polymer packing or decomposes on the polymer packing. Porous polymer column packings, therefore, cannot be used for determination of mixed-ligand complexes.

A column packing was prepared using Chromosorb W and 5% liquid coating of Kel-F-Wax, a chlorotrifluoroethylene polymer. Bleeding of the liquid phase was noted during conditioning of the column. Thermogravimetric analysis of a sample of the Kel-F-Wax revealed that the material begins to volatilize at between 150° and 175°C . This temperature range is not sufficiently high to allow use of this liquid phase for the determination of mixed-ligand complexes. A thermogram for another fluorine-containing liquid phase which was evaluated

is shown in Figure 4.1. The thermogram indicates that ZE7, a fluoroester, is non volatile up to about 225°C. A large number of GLC columns were made with packings coated with ZE7 and used for determination of metal complexes during the course of this thesis work. These columns were generally found to exhibit little interaction with metal complexes and sharp clean elution patterns were obtained.

During the last few months of this research project, it was observed that ZE7 bled from a column which was left conditioning overnight at 220°. This raised questions as to the thermal stability of ZE7 as a liquid phase. Shown in Figure 4.1 is a thermogram obtained at a constant temperature of 200°C with weight loss being measured as a function of time. These data indicate that ZE7 is volatilized at 200° under the flow conditions of a thermograph. It is likely that much more volatilization occurs at similar temperatures from a GLC column where the liquid phase is spread out over a very high surface area. Most of the GLC columns employing ZE7 as the liquid phase were conditioned at 200° to 220°C. These data indicate therefore, that all the chromatograms which were obtained on GLC columns using ZE7 for a liquid phase were in fact obtained on solid support with a very low amount of ZE7 present. This explains why very little interaction was

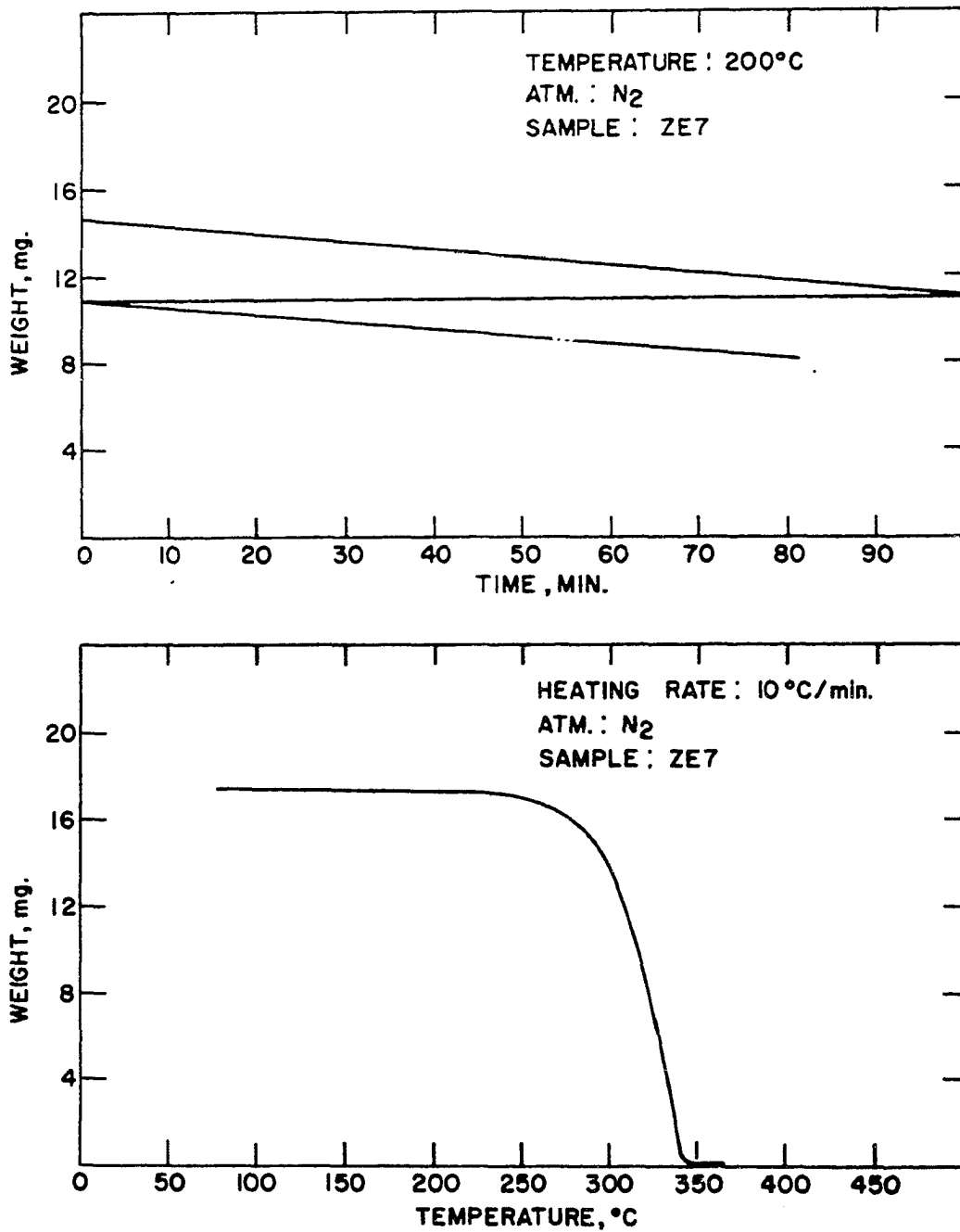


Figure 4.1. Thermograms for the liquid phase ZE7

observed between columns using ZE7 as the liquid phase and mixed-ligand complexes. Small amounts of ZE7 were undoubtedly retained on the active sites of the solid support which reduced tailing so that sharp chromatographic peaks were observed for the complexes determined.

The study of the ZE7 liquid phase exemplifies the helpfulness of thermoanalytical techniques in characterization of liquid phases and also illustrates that caution must be used in interpreting thermograms. The thermogram for ZE7 shown in Figure 4.1 indicates that ZE7 would not volatilize significantly at temperatures less than 225°C but the assumption that this was true lead to several false conclusions concerning the application of columns employing ZE7 as a liquid phase.

In summary, ZE7 apparently can be used to deactivate solid supports such as Chromosorb W or Chromosorb G. However, it cannot be maintained as a liquid phase on a GLC column at temperatures sufficiently high to allow determination of mixed-ligand complexes.

d. Silicone liquid phases The silicone liquid phases are the most widely used general purpose liquid phases (52). The silicone liquid phases are polysiloxanes which are characterized by the substituents used in the polymer. In this study SE30 which has methyl substituents, and QF-1 which has

methyl and some 1,1,1 trifluoropropyl substituents were evaluated. Figure 4.2 shows thermograms for SE30 and QF-1 which indicate these liquid phases to be non-volatile at temperatures as high as 300°C.

Both SE30 and QF-1 were found to be satisfactory liquid phases for GLC columns used to determine mixed-ligand complexes. These two liquid phases were stable at all required temperatures, provided resolution of the complexes from the components of the extraction mixtures and yielded high quality elution patterns. These silicone liquid phases were the only type of liquid phase studied which gave consistently good results in the determination of metal complexes.

2. Partitioning of mixed-ligand complexes with SE30 and QF-1

Since the silicone liquid phases appeared to be useful for the determination of mixed-ligand complexes, the partitioning of selected complexes by SE30 and QF-1 was studied in detail. Table 4.2 lists the column packings which were prepared for the study. A 4' x 1/4"-glass column was prepared from each packing. Glass columns were used as a matter of convenience. These studies indicated that either glass or stainless steel were suitable column materials.

Veening and Huber (142) studied the retention of metal

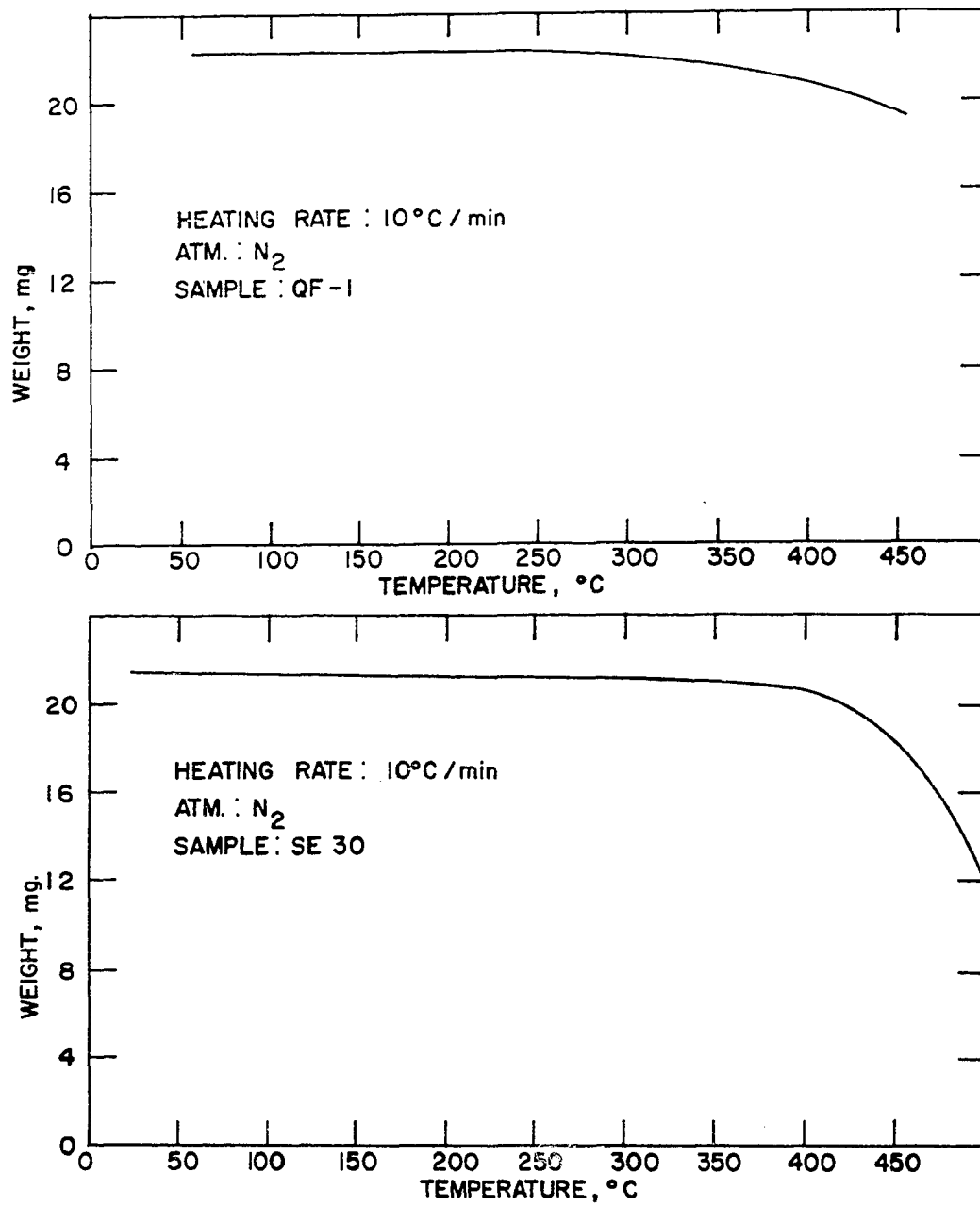


Figure 4.2. Thermograms for the liquid phases QF-1 and SE30

Table 4.2. Column packings prepared for study of partitioning of mixed-ligand complexes

Theory	% by weight on 100/120 mesh Chromosorb W	
	SE30	Found
		QF-1
1	0.95	1.1
5	4.9	4.5
10	10.0	9.9
20	19.1	17.8

chelates. They measured the partition ratio as a function of phase ratio for different chelates to determine the type of interaction occurring between metal chelates and a GLC column. The partition ratio, k , is related to the partition coefficient as shown in the following equation,

$$k = Kq \quad (4.1)$$

where K = partition coefficient and q = phase ratio or ratio of the volume of the stationary or liquid phase to the gas volume of the column. The partition coefficient and its relationship to retention behavior was discussed in Section I.

The partition ratio is easily obtained for a solute from the following equation,

$$k = (t_R - t_{R_0})/t_{R_0} \quad (4.2)$$

where t_R = retention time of the solute in minutes and t_{R_0} = retention time of an unretained solute such as air or methane in minutes. The partition ratio would be expected to increase

linearly with the phase ratio if gas-liquid partitioning is involved in the GLC column.

For this study, the partition ratio was determined and plotted versus the weight of liquid phase in the GLC column. The weight of liquid phase in the column is related to the phase ratio by the following constant, (density of liquid phase \times gas volume)⁻¹. Table 4.3 shows the mixed-ligand complexes which were used in this study. Retention times were obtained for each complex on each column at a series of temperatures ranging from about 150° to 220°C. Methane was used to determine the value of t_{R0} .

Table 4.3. Mixed-ligand complexes used in study of partitioning

Er(FHD) ₃ ·2TBP	Eu(FHD) ₃ ·2TBP	Nd(FHD) ₃ ·2TBP
Er(FHD) ₃ ·2DBSO	Eu(FHD) ₃ ·2DBSO	Nd(FHD) ₃ ·2DBSO
Er(FHD) ₃ ·2TBPO	Eu(FHD) ₃ ·2TBPO	Nd(FHD) ₃ ·2TBPO

Figure 4.3 shows a plot of the partition ratio for the complexes of erbium versus the weight of SE30 in different GLC columns. These data were obtained at a column temperature of 200°C. Similar results were obtained for the complexes of Eu and Nd with the exception that the complexes of Eu and Nd which contained TBPO could not be eluted at 200°C from the

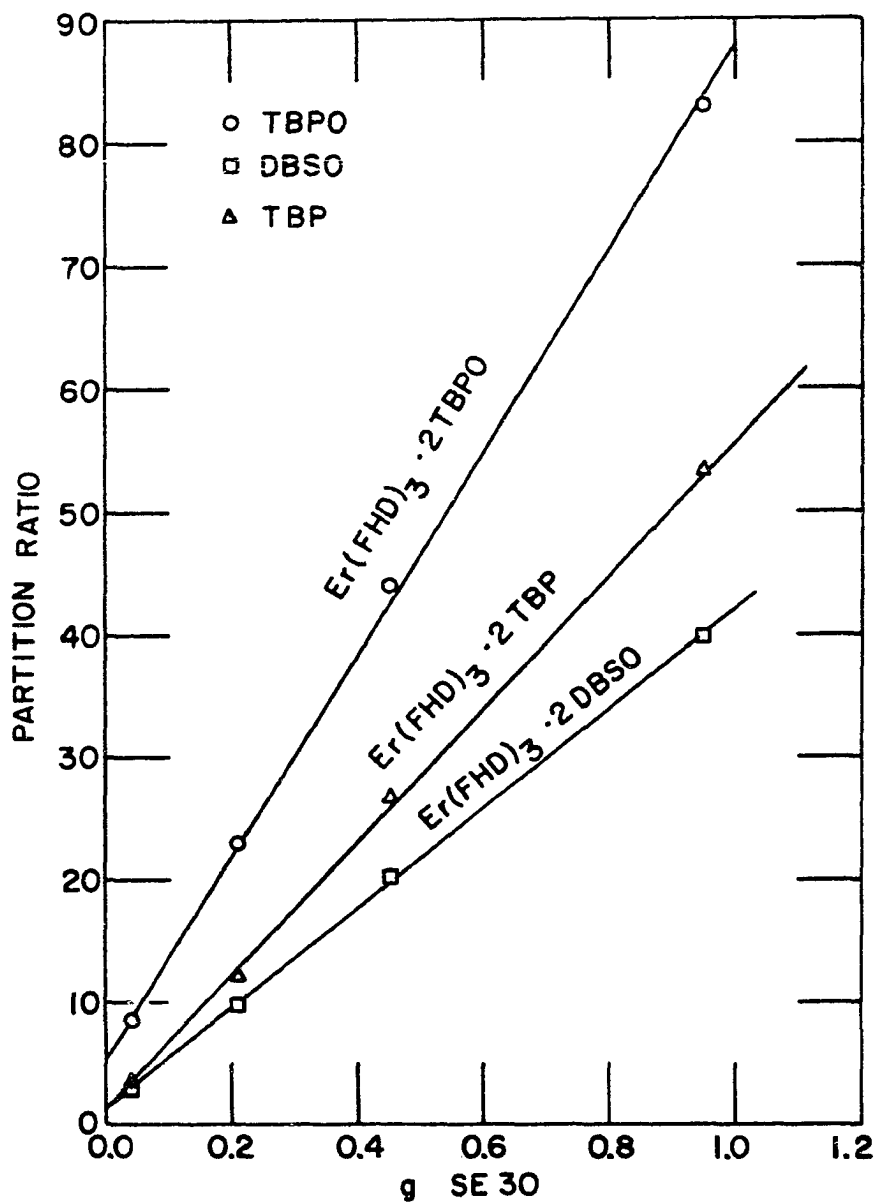


Figure 4.3. Dependence of the partition ratio on the amount of SE30 present in the GLC column

19.1% SE30 column (0.95g SE30). The linear variation of partition ratio with amount of liquid phase in the column indicates that gas-liquid partitioning is occurring between the mixed-ligand complexes and the liquid phase SE30. The data also show that the partitioning varies according to the neutral donor present, with the partitioning order being $TBPO > TBP > DBSO$. This same relative order of partitioning was observed for the complexes of Eu and Nd at this temperature. Data obtained for the retention of the complexes listed in Table 4.3 on SE30 columns indicated a partitioning of all the complexes in the order $TBPO > TBP > DBSO$ over the entire temperature range investigated.

Figure 4.4 shows a plot of the partition ratio for the complexes of erbium versus the weight of QF-1 in different GLC columns. These data were obtained at a column temperature of 200°C . As with the SE30 columns, similar results were obtained for the complexes of Eu and Nd. The linear increase of partition ratio with increase in the amount of liquid phase on the GLC column indicates that gas-liquid partitioning is occurring between the mixed-ligand complexes and the liquid phase QF-1. For the QF-1 columns, the data indicate the relative partitioning order for complexes with different neutral donors to be $TBPO > DBSO > TBP$. This

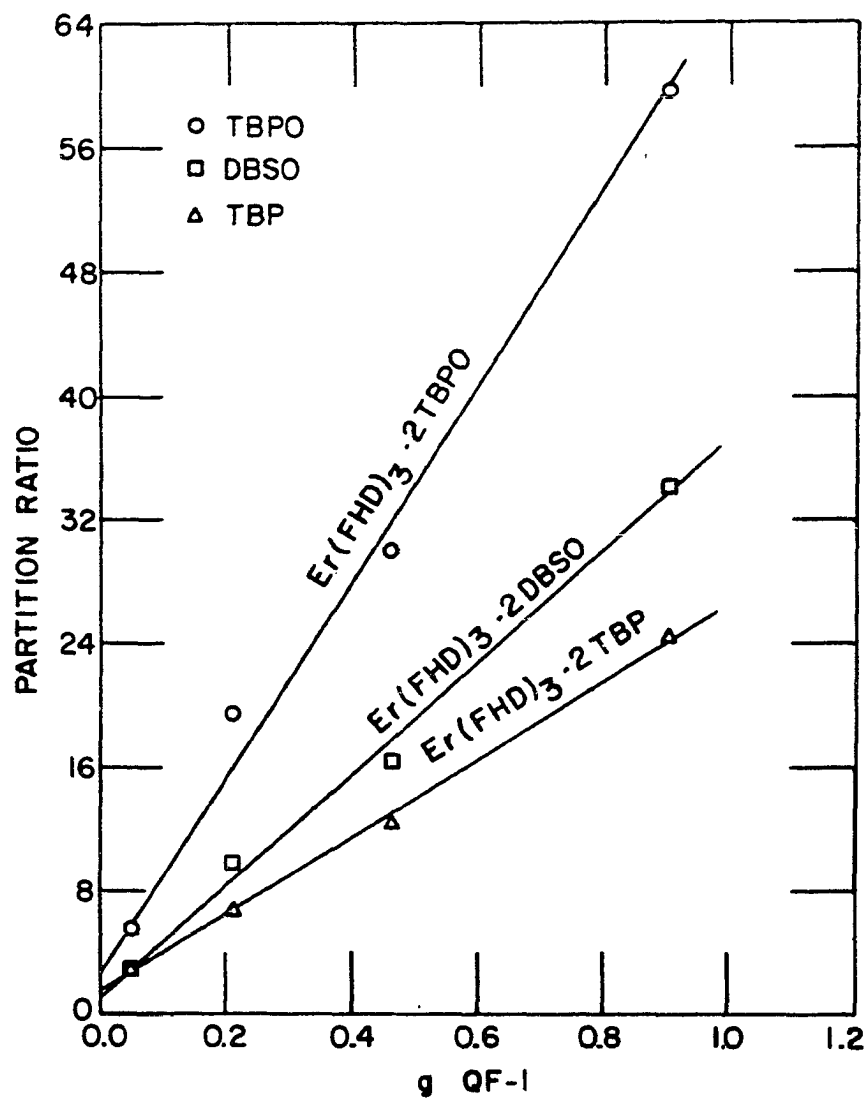


Figure 4.4. Dependence of the partition ratio on the amount of QF-1 present in the GLC column

relative partitioning order was observed for all the complexes listed in Table 4.3 over the entire temperature range investigated.

Shanker and Venkateswarlu (112) have studied the comparative donor properties of organic donors in solvent extraction. These workers reported the relative donor strength of the neutral donors used in the present study to be TBPO > DBSO > TBP. This order is the same as the relative partitioning order observed for the QF-1 columns. These data indicate the possibility that the neutral donor employed in the mixed-ligand complex contributes to the relative polarity of the extracted complex since the relative polarity of the donor is reflected in the relative partitioning order of the complexes on the liquid phase QF-1.

The difference in partitioning of mixed-ligand complexes is also reflected in the relative retention of complexes which contain different neutral donors. Figure 4.5 illustrates the relative retention of $\text{Eu}(\text{DODEFOD})_3 \cdot \text{TBP}$, $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{DBSO}$ and $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{TBPO}$ on a column using QF-1 as the liquid phase. These data show the relative retention order of the complexes to be TBPO > DBSO > TBP. The distorted peak for the TBPO complex shown in Figure 4.5 is due to column over-

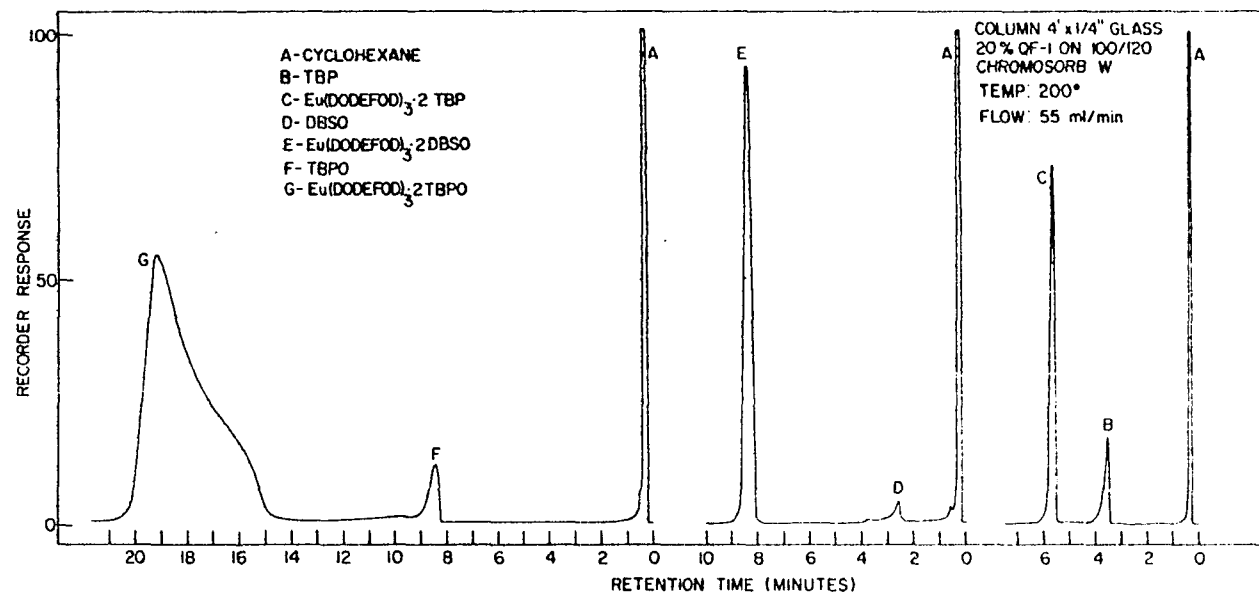


Figure 4.5. Gas chromatograms for $\text{Eu}(\text{DODEFOD})_3 \cdot 2 \text{ TBPO}$, $\text{Eu}(\text{DODEFOD})_3 \cdot 2 \text{ DBSO}$ and $\text{Eu}(\text{DODEFOD})_3 \cdot 2 \text{ TBP}$

loading.

Although variation in partition behavior as a function of the strength of the neutral donor may explain the relative order of retention observed on QF-1 columns, the data shown in Figure 4.3 indicate a different relative order on SE30 columns on which the complexes containing TBP partition more than those which contain DBSO. The reason for this shift in relative order is not understood. Such a shift is somewhat surprising in view of the chemical similarity of the liquid phases QF-1 and SE30. However, it is apparent that subtle differences in the interaction of these liquid phases with mixed-ligand complexes do exist.

Figures 4.3 and 4.4 both indicate non-zero intercepts for the family of curves showing the relation of the partition ratio for different mixed-ligand complexes to varying amounts of liquid phase. Veening and Huber (142) suggest that this observation indicates that some of the solutes are retained by the solid support used in the GLC column. If only the gas-liquid partition process were occurring, a zero intercept would be anticipated for these plots. As was discussed in Section I, a gas-solid interaction can be observed even when fairly high liquid loadings are employed.

The data given in Figures 4.3 and 4.4 also show higher

partition ratios for the mixed-ligand complexes on SE30 columns than for QF-1 columns with equivalent loadings. This is not surprising because the introduction of the fluorine containing moiety into the structure of the QF-1 liquid phase would be expected to decrease the interaction of this liquid phase with other chemical species.

In summary, the data discussed here indicate that mixed-ligand complexes are partitioned by the silicone liquid phases QF-1 and SE30. In addition some gas-solid interaction with the solid support Chromosorb W is indicated. These data indicate that the net retention, V_N' , of the mixed-ligand complexes on the columns utilizing the silicone liquid phases QF-1 and SE30 is a function of partition behavior of the complexes with the liquid phase, KV_L , and a function of adsorption by the solid support, $k_s A_s$, similar to the observations of Veening and Huber (142) for metal chelates.

3. Adsorption and displacement of mixed-ligand complexes

A persistent problem in the determination of metal complexes by G.C. has been that of adsorption by the GLC column of some of the metal complex. Workers in this research area have commonly reported the necessity of running several injections of a particular complex to condition the chromatographic

column (83,99,100,102,103). Uden and Jenkins (138) studied adsorption and displacement effects in the determination of Al(III), Cr(III) and Fe(III) β -diketonates. They observed that a metal chelate which had been adsorbed on the GLC column during determination by G.C. was subsequently displaced by the injection and elution of a chelate of another metal.

Figure 4.6 illustrates the adsorption and displacement of mixed-ligand complexes during determination by G.C. The chromatograms on the right in Figure 4.6 are for the separate determination of the complexes $\text{Er}(\text{HFA})_3 \cdot 2\text{DBSO}$ and $\text{Tb}(\text{HFA})_3 \cdot 2\text{DBSO}$. On the left of Figure 4.6 is a chromatogram for an injection of $\text{Th}(\text{HFA})_3 \cdot 2\text{DBSO}$ which was made following several determinations of the complex of Er. This chromatogram shows two gas chromatographic peaks for the metal complexes, one at about the retention time of the mixed-ligand complex of Er and the other at the retention time of the complex of Tb.

There are at least two possible explanations for the results observed here. The first is that some of the erbium complex is adsorbed and held up in the inlet or at the top of the GLC column. With injection of the terbium complex, the erbium complex is displaced and chromatographed with a reten-

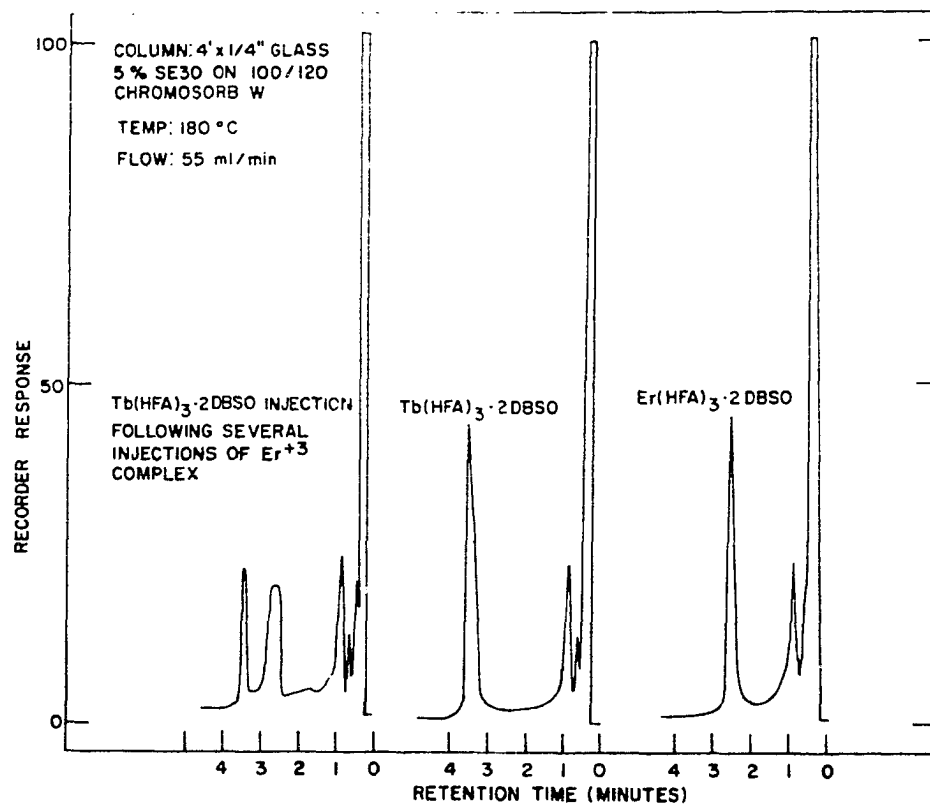


Figure 4.6. Gas chromatograms for the determination of $\text{Er}(\text{HFA})_3 \cdot 2\text{DBSO}$ and $\text{Tb}(\text{HFA})_3 \cdot 2\text{DBSO}$

tion time similar to a normal determination of the complex. A second possibility is that some of the erbium complex is adsorbed over the length of the column. With the injection of the terbium complex, the erbium complex is displaced continuously as the terbium complex passes through the column so that a displacement chromatogram is observed. In this case, the similarity of the retention time of the displaced species to that found upon normal injection of the complex is fortuitous.

This study indicates that the latter process is occurring. Several pieces of data support this. First, a series of determinations were carried out using on-column injection techniques and results similar to those shown in Figure 4.6 were obtained. These observations indicate that the injector is not involved in the adsorption of the complex. In addition, after several determinations of the erbium complex, the column was removed and switched end for end before the injection of the terbium complex. Again results similar to those shown in Figure 4.6 were obtained. These data indicate that the complex is not being adsorbed in the injector or on top of the column, but is being adsorbed over the length of the column and is displaced by the elution of another complex through the column.

Figure 4.7 shows apparent fluorescence spectra for a sample of the mixed-ligand complex $\text{Eu}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ which was trapped as eluted from the G.C. This sample was chromatographed after several determinations of $\text{Tb}(\text{DODEFOD})_3 \cdot 2\text{TBP}$. The existence of the apparent fluorescence spectra for both the terbium complex and the europium complex as shown in Figure 4.7 confirms that interchange of metal complexes is being observed and not some peculiar decomposition or interaction with the liquid phase of the column. Apparent fluorescence spectra were obtained which confirmed a similar exchange for the mixed-ligand complexes of Sm and Eu, Sm and Tb, and Tb and Eu with $\text{H}(\text{DODEFOD})$ and TBP, and with $\text{H}(\text{FHD})$ and TBP.

Table 4.4 shows the peak heights for a series of injections of HFA-TBP complexes. It was observed that complexes of Sm gave an unusually large response on the flame ionization detector (this phenomena will be discussed in Section V). The data presented in Table 4.4 indicate the response of the flame detector to the complex of terbium is enhanced after the complex of Sm has been determined on the column. These data are in accord with the observations discussed above concerning adsorption and displacement of mixed-ligand complexes. It would appear that some of the complex of Sm is adsorbed on the column and subsequently displaced with the complex of Tb

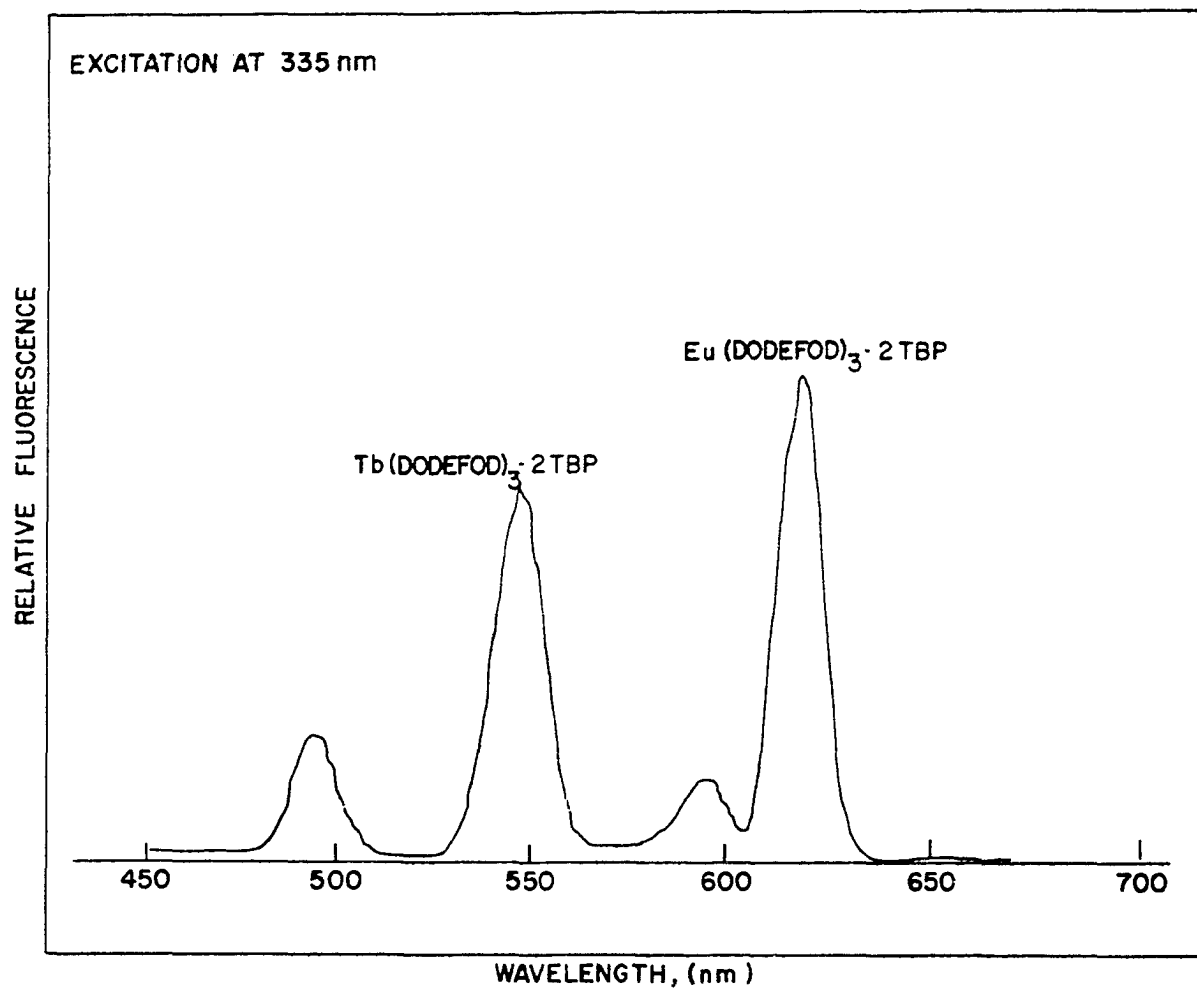


Figure 4.7. Apparent fluorescence spectra for Tb(DODEFOD)₃ · 2TBP and Eu(DODEFOD)₃ · 2TBP

Table 4.4. Determination of the mixed-ligand complexes of Tb and Sm with H(HFA) and TBP

Column: 4' x 1/4"-glass packed with 5% SE30 on Chromosorb W

Column temperature: 200°C

Attenuation: 5×10^5

Sample size: 1 μ l of ~ 0.007 M complex

Run no.	HFA-TBP	Peak height
1	Tb	4.9
2	Sm	off scale
3	Sm	off scale
4	Tb	9.1
5	Tb	8.0
6	Tb	7.2
7	Tb	6.6
8	Tb	6.1
9	Tb	5.6
10	Tb	5.3

resulting in an increased detector response for the complex of Tb. These data indicate that the displacement of an adsorbed complex may occur for several determinations after a particular complex has been adsorbed. This was also observed for the case shown in Figure 4.6. If several determinations of the complex of Tb were made after the determination of the complex of Er, the peak observed for the erbium complex grew smaller and smaller until after 6 or 7 injections of the terbium complex, the apparent erbium peak disappeared.

The interchange of $\text{Eu}(\text{FHD})_3 \cdot 2\text{TBP}$ and $\text{Tb}(\text{FHD})_3 \cdot 2\text{TBP}$ was studied for all the columns made from the packings listed in

Table 4.2. On the newly conditioned column, 2 μ l samples of ~ 0.01 M Eu complex were injected until the chromatographic peak for the complex could be seen. Then a 2 μ l sample of Tb complex was injected and the complex was trapped as eluted from the G.C. The apparent fluorescence spectra were obtained for these trapped samples and the relative intensity of the fluorescence of the Eu and Tb complexes were compared. These data did not indicate a significant difference in the exchange of the Eu and Tb complexes as a function of the liquid loading of the GLC column. However, it was noted that 2 or 3 sample injections were needed before the first peak for the complex could be observed from a column with 1% liquid loading while the columns with 20% liquid phase gave a peak for the complex on the first injection. These data give some indication that most of the adsorption of the mixed-ligand complexes occurs on the solid support.

The existence of these adsorption and displacement effects in the determination of mixed-ligand complexes of the lanthanides by G.C. means that caution must be exercised in the interpretation of gas chromatographic results. The column history may be a very important factor in interpreting the results of any particular determination of metal com-

plexes by G.C.

4. Separation of mixed-ligand complexes and column over-loading

The feasibility of separation of mixed-ligand complexes has been demonstrated in Section III and illustrated in Figure 3.33 which shows the separation of the mixed-ligand complexes of Th(IV) and UO_2^{+2} with H(HFA) and TBP. For this determination a short column using a packing with high liquid loading was used. A general characteristic observed for the determination of metal complexes by G.C. is that column efficiency for these species is lower than for simple volatile organic substances of comparable volatility (138). This is in part due to the fact that the gas chromatographic peaks obtained for metal complexes tend to have exceptionally wide half-widths. As a result it is not feasible to try to gain resolution by use of longer columns because the peak widths become larger and larger as the column is lengthened.

Hence, for packed GLC columns it seemed reasonable that the best separations could be obtained with short columns which contained packing with a high percentage of liquid phase. This combination might achieve maximum partitioning with the high percentage of liquid phase, while not getting peaks which were too broad.

Figure 4.8 shows the separation of $\text{Er}(\text{FHD})_3 \cdot 2\text{DBSO}$ and $\text{Tb}(\text{FHD})_3 \cdot 2\text{DBSO}$ on a 2' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 20% QF-1. This separation required a step temperature program as indicated in Figure 4.8 to achieve reasonable peak shapes. Attempts to duplicate this separation on a 4' x 1/4"-column packed with 20% QF-1 on Chromosorb W and a similar column packed with 5% QF-1 on Chromosorb W were not successful. Glass columns (4' x 1/4") packed with 5% SE30 on Chromosorb and 20% SE30 on Chromosorb W were also tried, and separation of these complexes could not be achieved. Characteristically, for the longer columns the chromatographic peaks for the complexes were much broader and overlapped.

Figure 4.9 shows a chromatogram for the separation of $\text{Er}(\text{FHD})_3 \cdot 2\text{TBPO}$, $\text{Tb}(\text{FHD})_3 \cdot 2\text{TBPO}$, $\text{Nd}(\text{FHD})_3 \cdot 2\text{TBPO}$ and $\text{La}(\text{FHD})_3 \cdot 2\text{TBPO}$ on a 2' x 1/4"-glass column packed with 100/120 mesh Chromosorb W coated with 20% QF-1. This separation also required a step program as is indicated in Figure 4.9. Attempts to repeat this separation on longer columns using QF-1 or SE30 as the liquid phase were not successful.

For the mixed-ligand complexes, better separations could be achieved with the complexes using TBPO as would be expected from the partition data shown in Figures 4.3 and 4.4. How-

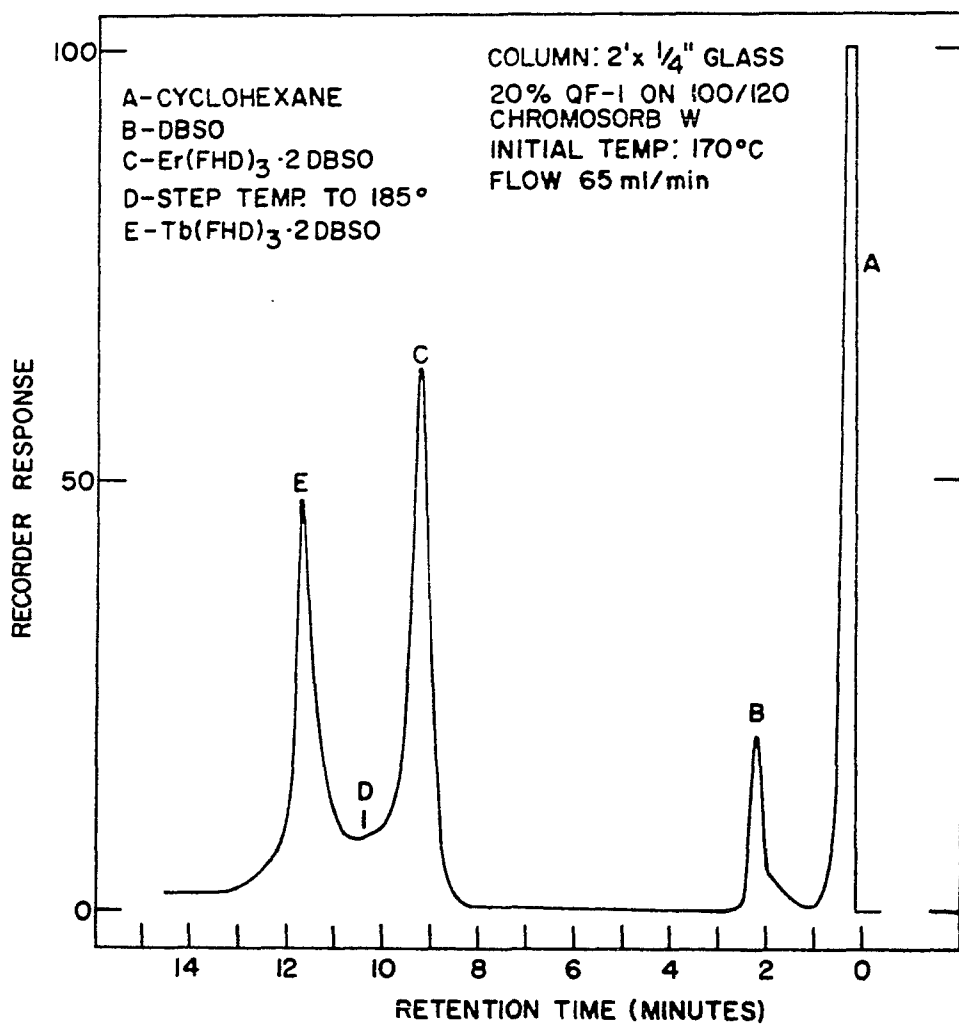


Figure 4.8. Gas chromatogram of a mixture of $\text{Er}(\text{FHD})_3 \cdot 2\text{DBSO}$ and $\text{Tb}(\text{FHD})_3 \cdot 2\text{DBSO}$

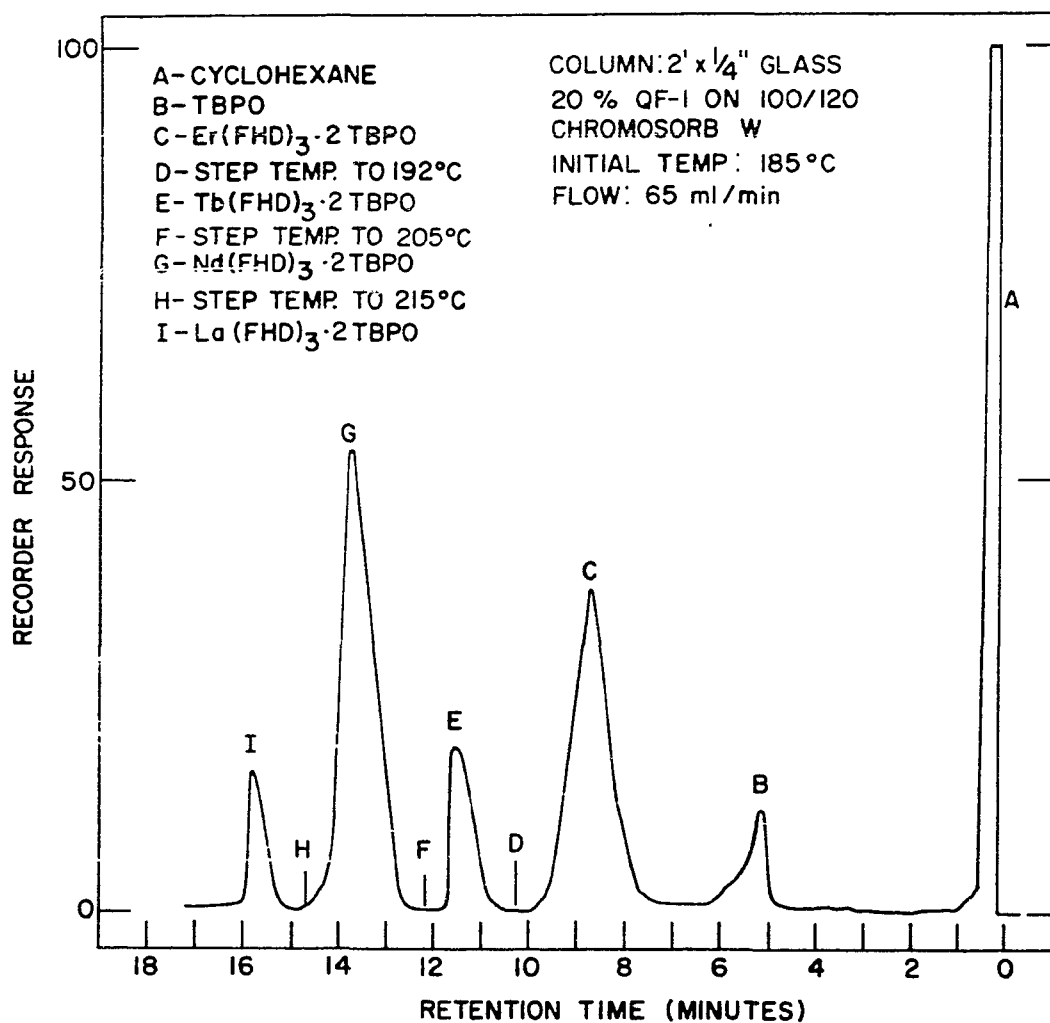


Figure 4.9. Gas chromatogram of a mixture of Er(FHD)₃·2TBPO, Tb(FHD)₃·2TBPO, Nd(FHD)₃·2TBPO and La(FHD)₃·2TBPO

ever, it was found that for GLC columns which highly partitioned the TBPO complexes, the excess TBPO in the extraction mixture was not well resolved from complexes of Tm, Yb and Lu. This fact limits the combinations of mixed-complexes of the lanthanides which can be resolved using the TBPO complexes.

An additional problem in the separation of mixed-ligand complexes of the lanthanides on packed GLC columns is that the sample size which can be handled is severely limited by column overloading. Figure 4.10 shows two chromatograms for $\text{Dy}(\text{FHD})_3 \cdot 2\text{TBPO}$. The first chromatogram is for a $2.0 \mu\text{l}$ injection of $\sim 0.01 \text{ M}$ complex while the second is for a $0.4 \mu\text{l}$ injection of the same complex. In this study, multiple peaks, leading edges or otherwise distorted gas chromatographic peaks were commonly observed when the capacity of the GLC column was exceeded. The data shown in Figure 4.10 graphically illustrate this problem which was often observed throughout the course of this research on mixed-ligand complexes. The limited capacity of packed GLC columns for mixed-ligand complexes severely limits the range of concentrations of mixed-ligand complexes and the number of these complexes which can be separated and determined by G.C.

A study was made of the retention times for the complexes

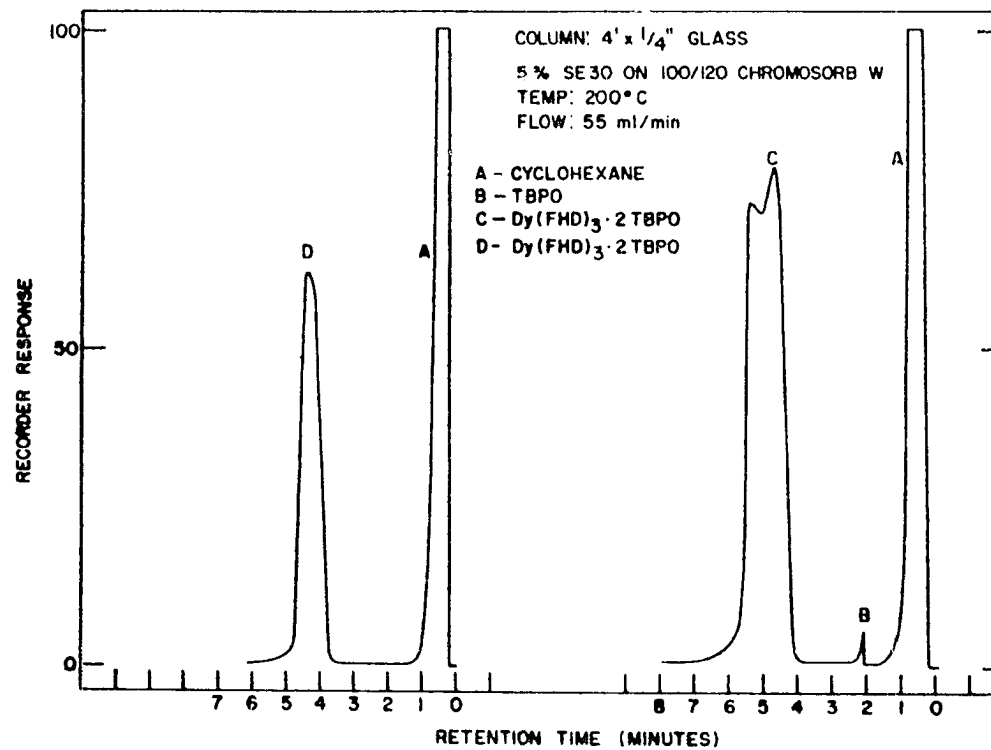


Figure 4.10. Gas chromatograms for Dy(FHD)₃ · 2TBPO

$\text{Nd}(\text{DODEFOD})_3 \cdot 2\text{TBPO}$, $\text{Nd}(\text{DODEFOD})_3 \cdot 2\text{DBSO}$, and $\text{Nd}(\text{DODEFOD})_3 \cdot 2\text{TBP}$ as a function of solute concentration. These data indicate that the retention time varies as a linear function of the amount of complex present as solute. As was discussed in Section I, such a variation implies a non-equilibrium situation where the concentration of solute in the liquid phase divided by the concentration of solute in the gas phase is not a constant. It is apparent from the work reported in this thesis that very small samples of mixed-ligand complexes must be used if this non-equilibrium situation is to be avoided.

Packed GLC columns can be used for separation of mixed-ligand complexes of the lanthanides. However, the existence of adsorption and displacement effects, of relatively poor column efficiency, and of the low capacity of these columns for mixed-ligand complexes indicates that these columns are of limited value for determination of more than 4 or 5 selected lanthanides at a time. Determinations of mixed-ligand complexes on packed GLC columns must be done with great care to insure that adsorption and displacement effects are not interfering with the analysis.

V. AN INVESTIGATION OF THE PERFORMANCE OF GAS
CHROMATOGRAPHIC DETECTORS IN THE DETERMINATION OF MIXED-
LIGAND COMPLEXES

A. Introduction

It is the purpose of these experiments to evaluate the performance of the flame ionization detector (FID) and the thermal conductivity (TC) detector for the determination of mixed-ligand complexes. It has been documented that the FID and/or the TC detector do not give equivalent response for different chemical species (22). Hill and Gesser (51) have shown that the response of the flame ionization detector varies as a function of the metal for the simple chelates of H(HFA). If quantitative determinations are to be made by G.C., the response characteristics of the detector for the various species being determined must be known. In addition, any limitations due to the sensitivity of the detector which may effect column performance or other aspects of the determination by G.C. should be understood.

B. Experimental

1. Apparatus

a. Gas chromatographs The studies of the flame ionization detector were performed on a Beckman GC-4 gas

chromatograph equipped with an on-column inlet, flash-vaporization inlet, and hydrogen flame ionization detector. The chromatograms were recorded with a Bristol model 560 Dynamaster recorder equipped with a Disc integrator. The studies of the thermal conductivity detector were performed on a Hewlett-Packard Model 5756B equipped with a flash-vaporization inlet. The chromatograms were recorded in a Hewlett-Packard recorder, Model 7128A. High-purity helium supplied by the Matheson Company was used as a carrier gas for both chromatographs.

b. Fluorimeter Fluorescence data were taken on an Aminco-Bowman Spectrophotofluorimeter equipped with a Moseley X-Y recorder.

2. Metal complexes

a. Mixed-ligand complexes The mixed-ligand complexes of the lanthanides were prepared by solvent extraction. The solvent extraction procedure has been discussed in Section III.

b. Metal chelates Lanthanide chelates with H(THD) were prepared according to the procedure of Eisentraut and Sievers (29). 2,2,6,6-tetramethyl-3,5-heptanedione, H(THD), was obtained from Peninsular Chem Research and redistilled

before use.

C. Results and Discussion

Butts (14) reported that the response of the flame ionization detector for $\text{Eu}(\text{HFA})_3 \cdot 2\text{TEP}$ was greater than that of $\text{Tm}(\text{HFA})_3 \cdot 2\text{TBP}$ by a factor of about two, however, no comparison was reported for the other lanthanide complexes. Figure 5.1 shows a bar graph which illustrates the response of the FID for 1 μl injections of 0.007 M mixed-ligand complexes of the lanthanides and yttrium with H(DCDEFOD) and TBP. These data indicate a response for the samarium complex which is from 5 to 50 times greater than that for any of the other complexes studied. Figure 5.2 shows a bar graph which illustrates the response of the FID for complexes of the lanthanides and yttrium with H(DODEFOD) and DBSO. Again the samarium complex is seen to exhibit an unusually large response relative to the other complexes. The overall response of the FID to the complexes containing DBSO is less than the response for the complexes containing TBP. This is to be expected since the FID responds well to the methylene moiety ($-\text{CH}_2-$) and TBP contributes eight more methylene moieties to each mixed-ligand complex than does DBSO.

Figure 5.3 shows a bar graph for the FID response of the

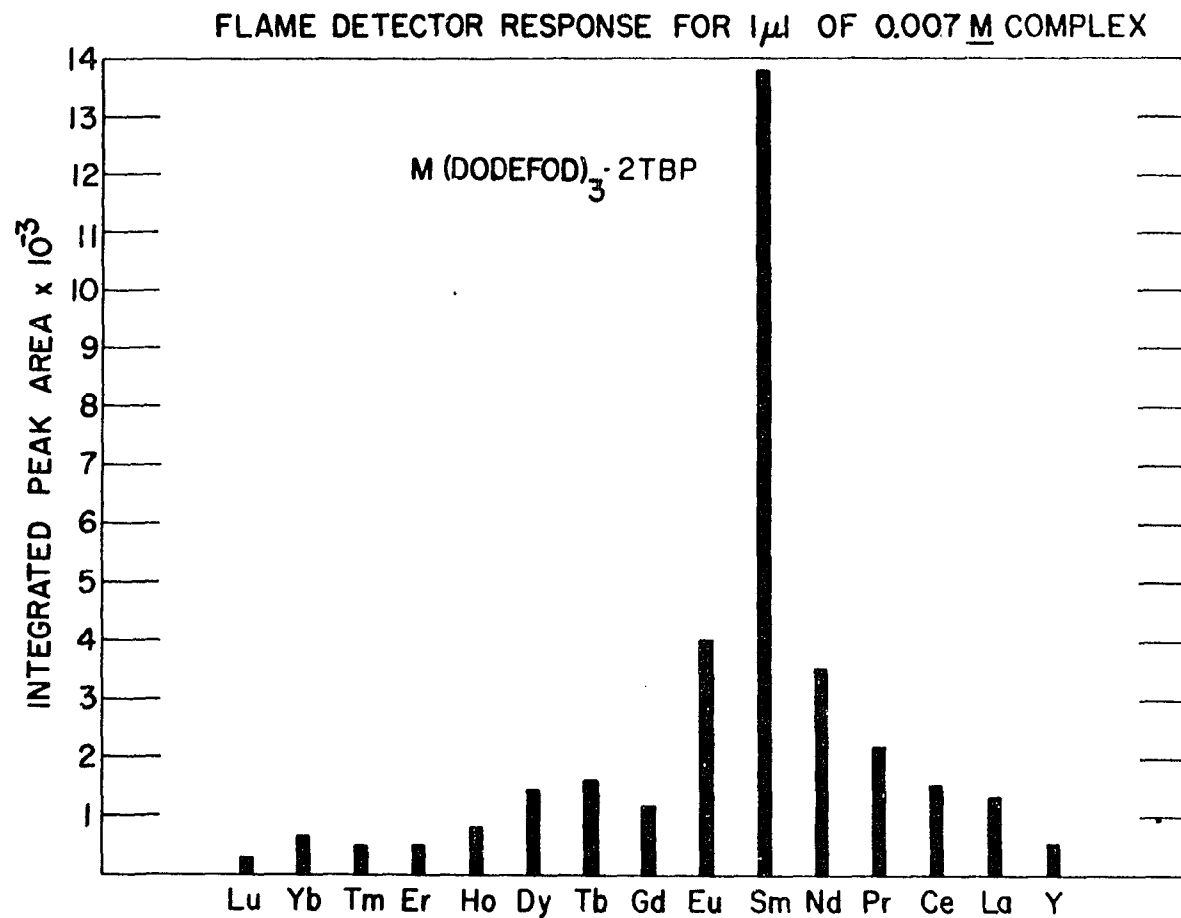


Figure 5.1. Flame ionization detector response for mixed-ligand complexes of the lanthanides and yttrium with H(DODEFOD) and TBP

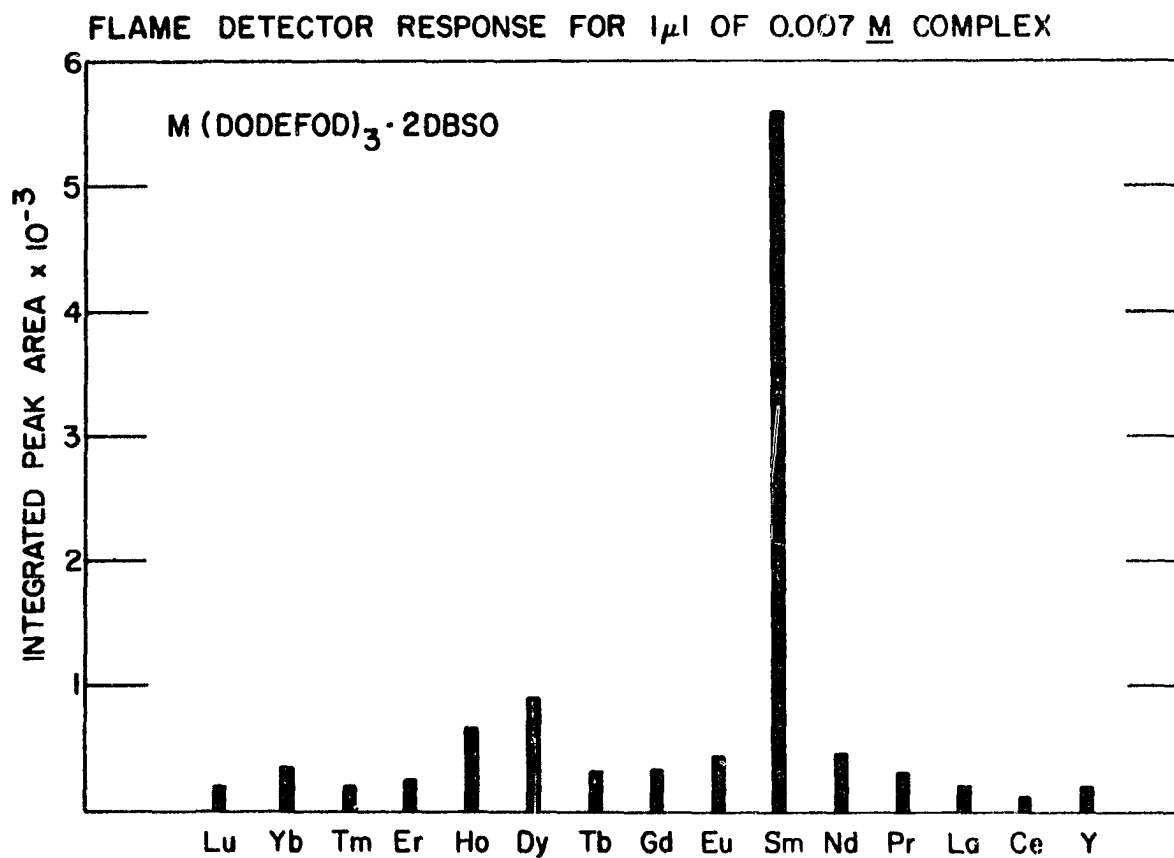


Figure 5.2. Flame ionization detector response for mixed-ligand complexes of the lanthanides and yttrium with H(DODEFOD) and DBSO

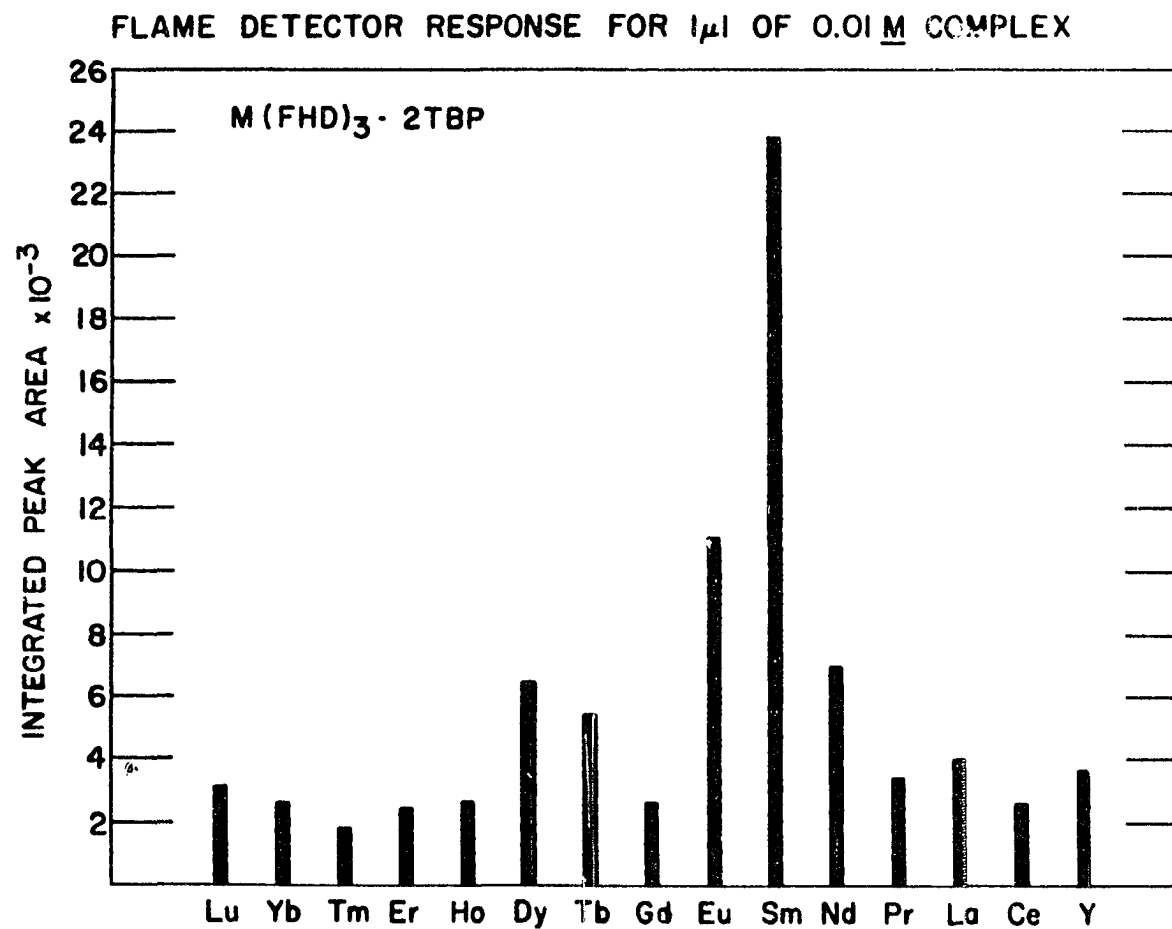


Figure 5.3. Flame ionization detector response for mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBP

complexes of the lanthanides and yttrium with H(FHD) and TBP. Again significant variation of detector response as a function of the metal is observed with the samarium complex yielding an unusually large response. Data reported in Section III confirms that $\text{Sm}(\text{FHD})_3 \cdot 2\text{TBP}$ is eluted intact from the chromatograph. Figure 3.23 shows apparent fluorescence spectra which confirm that $\text{Sm}(\text{FHD})_3 \cdot 2\text{DBSO}$ is eluted from the gas chromatograph. Similar data were obtained for the complexes $\text{Sm}(\text{FHD})_3 \cdot 2\text{TBP}$ and $\text{Sm}(\text{FHD})_3 \cdot 2\text{TBPO}$. The data imply, therefore, that there is some peculiar behavior in the combustion of the samarium complex in the FID which results in production of an unusually large ion current.

Table 5.1 lists the complexes of samarium which were determined on the FID of the gas chromatograph and found to give an unusually large response relative to similar complexes with other lanthanide metals. The variety of β -diketones and neutral donors employed in this study furnish evidence that the unusual response of the FID is not related to the β -diketone or the neutral donor employed in the complex. These data indicate that the variation in FID response to the mixed-ligand complexes of the lanthanides is related to the particular metal in the complex and not related to the other chemical

Table 5.1. Complexes of samarium which exhibit unusual response on flame ionization detectors

$(\text{FOD})_3 \cdot 2\text{TBP}$	$(\text{DODEFOD})_3 \cdot 2\text{DBSO}$
$(\text{HFA})_3 \cdot 2\text{TBP}$	$(\text{DODEFOD})_3 \cdot 2\text{TBPO}$
$(\text{HFA})_3 \cdot 2\text{DBSO}$	$(\text{FHD})_3 \cdot 2\text{TBP}$
$(\text{MFOD})_3 \cdot 2\text{TBP}$	$(\text{FHD})_3 \cdot 2\text{DBSO}$
$(\text{DECAFHD})_3 \cdot 2\text{TBP}$	$(\text{FHD})_3 \cdot 2\text{TBPO}$
$(\text{DODEFOD})_3 \cdot 2\text{TBP}$	$(\text{THD})_3$

components of the complex. The reasons for this FID response variation are not understood.

In view of the adsorption and displacement phenomena discussed in Section IV, it is clear that great care must be taken if the FID is to be used for determination of mixed-ligand complexes of the lanthanides. The displacement of a complex of samarium, with its high FID response, along with another complex could totally distort the measured response for a particular complex. Hence it is clear that the FID is of limited value as a means of detecting mixed-ligand complexes of the lanthanides as they are eluted from a gas chromatograph.

Table 5.2 indicates some relative areas for some selected mixed-ligand complexes on the TC detector. These areas have

Table 5.2. Integrator counts for the response of a thermal conductivity detector for a 1 μ l injection of 0.01 M complex

Complex	Integrator counts
Tm(FHD) ₃ · 2TBP	4
Ho(FHD) ₃ · 2TBP	4
Tb(FHD) ₃ · 2TBP	4
Eu(FHD) ₃ · 2TBP	9
Sm(FHD) ₃ · 2TBP	6
Pr(FHD) ₃ · 2TBP	9

been normalized for a 1 μ l injection of mixed-ligand complexes so that the areas correspond to those shown in Figure 5.3 for the FID response. There is some variation in the response of the TC detector to mixed-ligand complexes. However, the complexes which exhibited a higher average response on the TC detector were those of Eu, Sm, Nd, Pr and Ce. In every case, the chromatographic peaks for these complexes were distorted with a significant leading edge. This distortion makes the measurement of peak area less precise and raises some question as to the significance of the indicated area differences. It was not possible to avoid serious overloading of the GLC column when a TC detector was used. Ten to fifteen microliter

injections of 0.01 M complex were necessary to obtain a measurable chromatographic peak. These data indicate that the TC detector is not useful for the determination of mixed-ligand complexes. Although the response variations on the TC detector for the complexes of different metals is not a significant problem, the total response of the TC detector is not adequate to allow use of sample sizes which will not severely overload the GLC column.

VI. SUMMARY

The lanthanides and yttrium can be determined by G.C. as mixed-ligand complexes. Complexes of the lanthanides and yttrium of stoichiometry $ML_3 \cdot 2Y$, where M = metal ion, L = β -diketone and Y = neutral donor, have been prepared by solvent extraction and determined by G.C. Several combinations of mixed extractants which give mixed-ligand complexes of the lanthanides that are thermally stable and volatile have been identified. The β -diketones 1,1,1,2,2,3,3,6,6,7,7,7-dodecafluoro-4,6-octanedione, H(DODEFOD), or 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione, H(FHD), in combination with the neutral donors tri-n-butylphosphate, TBP, di-n-butylsulfoxide, DBSO, or tri-n-butylphosphine oxide, TBPO, have been found to form mixed-ligand complexes of the lanthanides which can be eluted from the gas chromatograph intact as the $ML_3 \cdot 2Y$ complex at a temperature of about 200°C. The fully fluorinated heptane or octanediones yield mixed-ligand complexes which are thermally stable and give better elution patterns than β -diketones which contain alkyl side chains such as H(MFOD) or the smaller fluorinated β -diketones such as H(HFA).

Mixed-ligand complexes of UO_2^{+2} and Th(IV) with H(HFA) and DBSO can be separated and determined quantitatively by

G.C. Detection limits were found to be 0.4 mg/ml for thorium and 0.6 mg/ml for uranium.

Mixed-ligand complexes of the lanthanides are partitioned by the silicone liquid phases SE30 and QF-1 on packed GLC columns. Short GLC columns with 10 to 20% silicone liquid phase can be used to separate some mixtures of mixed-ligand complexes of the lanthanides. However, the existence of adsorption and displacement effects and the low capacity of the packed GLC columns for mixed-ligand complexes severely limit the use of packed columns for the separation of mixed-ligand complexes.

The flame ionization detector responds to mixed-ligand complexes of the lanthanides as a function of the individual metal. Samarium complexes produce an unusually large response on the flame ionization detector. The wide variation of response of the flame ionization detector to mixed-ligand complexes make it unsuitable for determination of mixtures of metal complexes. The thermal conductivity detector is not sensitive enough to mixed-ligand complexes to allow determination of samples which do not exceed the capacity of the gas chromatographic column.

VII. SUGGESTIONS FOR FUTURE WORK

Mixed-ligand complexes utilizing fluorinated β -diketones and neutral donors such as TBP, DBSO and TBPO appear to be easily extracted and easily determined by G.C. It would be of interest to investigate complexes other than those of the lanthanides, such as divalent transition metals, which may be able to be determined by G.C. as mixed-ligand complexes.

Investigation of open tubular columns coated with SE30 or QF-1 may be of value in extending the ability to separate mixed-ligand complexes of the lanthanides. Open tubular columns may not show the adsorption and displacement effects found for packed columns and should be more efficient than packed columns.

The electron capture detector should be investigated as an alternative to the FID and TC detector for the determination of mixed-ligand complexes. The electron capture detector will allow significantly lower detection limits for complexes such as those of UO_2^{+2} and Th(IV). In addition the electron capture detector may not exhibit such wide response variations as does the FID. It would also be of interest to study the flame chemistry associated with the combustion of mixed-ligand complexes of samarium in an effort to determine the reasons for the unusual FID response to these complexes.

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IX. APPENDIX

Structure and nomenclature

Name	Abbreviation	Structure
2,4-pentanedione	H(ACAC)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CH}_3\text{C}=\text{CHCCH}_3 \end{array}$
1,1,1-trifluoro-2,4-pentanedione	H(TFA)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CF}_3\text{C}=\text{CHCCH}_3 \end{array}$
1,1,1,5,5,5-hexafluoro-2,4-pentanedione	H(HFA)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CF}_3\text{C}=\text{CHCCF}_3 \end{array}$
1,1,1,2,2,3,3-heptafluoro-7-methyl-4,6-octanedione	H(MFOD)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CF}_3\text{CF}_2\text{CF}_2\text{C}=\text{CHCCH}(\text{CH}_3)_2 \end{array}$
1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione	H(DECAFHD)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CF}_3\text{CF}_2\text{CF}_2\text{C}=\text{CHCCF}_3 \end{array}$
1,1,1,2,2,3,3,7,7,8,8,8-dodecafluoro-4,6-octanedione	H(DODEFOD)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CF}_3\text{CF}_2\text{CF}_2\text{C}=\text{CHCCF}_2\text{CF}_3 \end{array}$
1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione	H(FHD)	$\begin{array}{c} \text{OH} \quad \text{O} \\ \quad \parallel \\ \text{CF}_3\text{CF}_2\text{C}=\text{CHCCF}_2\text{CF}_3 \end{array}$

Name	Abbreviation	Structure
1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione	H(FOD)	$\text{CF}_3\text{CF}_2\text{CF}_2\overset{\text{OH}}{\underset{ }{\text{C}}}=\overset{\text{O}}{\parallel}\text{CHCC}(\text{CH}_3)_3$
2,2,6,6-tetramethyl-3,5-heptanedione	H(THD)	$(\text{CH}_3)_3\overset{\text{OH}}{\underset{ }{\text{C}}}\overset{\text{O}}{\parallel}=\text{CCC}(\text{CH}_3)_3$
1,1,1-trifluoro-6,6-dimethyl-2,4-heptanedione	H(PTA)	$\text{CF}_3\overset{\text{OH}}{\underset{ }{\text{C}}}=\overset{\text{O}}{\parallel}\text{CHCC}(\text{CH}_3)_3$
Tri- <u>n</u> -butyl phosphate	TBP	$(\text{C}_4\text{H}_9\text{O})_3\text{-P}\rightarrow\text{O}$
Tri- <u>n</u> -butylphosphine oxide	TBPO	$(\text{C}_4\text{H}_9)_3\text{-P}\rightarrow\text{O}$
Tri- <u>n</u> -octylphosphine oxide	TOPO	$(\text{C}_8\text{H}_{17})_3\text{-P}\rightarrow\text{O}$
Tri-phenylphosphine oxide	TPPO	$(\text{C}_6\text{H}_5)_3\text{-P}\rightarrow\text{O}$
Methylenebis(di- <u>n</u> -hexylphosphine oxide)	MHDPO	$(\text{C}_6\text{H}_{13})_2\overset{\text{O}}{\underset{ }{\text{P}}}\text{-CH}_2\text{-}\overset{\text{O}}{\underset{ }{\text{P}}}\text{-}(\text{C}_6\text{H}_{13})_2$
Di- <u>n</u> -butylsulfoxide	DBSO	$(\text{C}_4\text{H}_9)_2\text{-S}\rightarrow\text{O}$
Dimethylsulfoxide	DMSO	$(\text{CH}_3)_2\text{-S}\rightarrow\text{O}$

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