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Gas chromatographic determination of lanthanide mixed-ligand complexes of 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione

Charles Allen Burgett
Iowa State University

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Gas chromatographic determination of lanthanide mixed-ligand complexes of 1, 1, 1, 2, 2, 6, 6, 7, 7, 7-decafluoro-3, 5-heptanedione

by

Charles Allen Burgett

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I. LITERATURE REVIEW AND THEORY

A. Introduction

This thesis will report the comprehensive study of the various factors which contribute to the development of an analytical method for cationic species by gas chromatography. Synergistic solvent extraction systems which form mixed-ligand complexes suitable for gas chromatographic determinations, various column phenomena, chromatographic detectors, and interferences have been studied. A new series of paramagnetic shift reagents for nuclear magnetic resonance has been developed and systematically evaluated. The review of the literature will necessarily be restricted only to those areas directly pertinent to these topics.

The vast majority of inorganic gas chromatography has been performed with systems involving metal chelates; for this reason the literature review will cover only such systems. This section will also include discussion of the literature and theory of solvent extraction as it applies to the mixed-ligand complexes evaluated in this study.

The literature review and theory concerning gas chromatographic columns will be related only to the chromatography of metal complexes and the phenomena observed during metal analysis by gas chromatography.

As a result of the voluminous literature concerning the application of paramagnetic shift reagents to nuclear magnetic resonance, this literature review will be restricted to the chemical nature of the shift reagents presently utilized.

B. Chemical Systems for the Gas Chromatography of Cationic Species

Since the initial studies of James and Martin (74, 75), gas chromatography has revolutionized separations in organic and biochemistry.

The development of inorganic gas chromatography has been relatively slow in coming; however, the inherent advantages of extraordinary sensitivity and speed and ease of separating mixtures of closely related compounds, has promoted a recent surge of interest in the technique. In general, gas chromatographs are not conveniently operated at temperatures in excess of 350°C. This temperature requirement places severe limitations on the types of inorganic compounds that can be chromatographed. In most, but not all cases, the metal complex must exhibit a vapor pressure of 0.1 to 1 mm of mercury in order to have a reasonable rate of gas-phase migration through the column (154). To meet the requirement, the complexes must be unusually volatile and thermally stable in the chromatographic column. Metal compounds of suitable volatility are limited in number and include metal alkyls, metal alkoxides, metal carbonyls, metal hydrides, metal halides, π-bonded metal complexes and β-diketonates (113, 154). Furthermore, the compounds must be formed in quantitative yield to be of practical analytical utility. The metal halides and the metal β-diketonates are the only two of the above which meet all these requirements.

Pommier (120) has reviewed the determination of inorganic halides by gas chromatography up to 1966 and Anvaer and Drugov (4) have reviewed the literature from 1963 to 1970. Although many techniques have been developed and employed, the utility of metal analysis as metal halides is limited by the difficulty in synthesis and sample handling.

The volatility of metal acetylacetonates was first described by Morgan and Moss in 1914 (108). In 1955 Lederer (86) first suggested gas chromatography of metals as chelates of acetylacetone, but it was not until 1959 that Duswalt (41) actually chromatographed the acetylacetonates of beryllium, zinc, and scandium. Simultaneously, Biermann and Gesser (21) reported the successful elution of berylium, aluminum and chromium as complexes of acetylacetone. Although some success was achieved, the majority of the acetylacetonates are not sufficiently volatile and thermally stable to be chromatographed in the gas phase. In 1963 Sievers et al. (158) published a paper describing the gas chromatography of several metal chelates of acetylacetone (HACAC)[1], trifluoroacetylacetone (HTFA) and hexafluoroacetylacetone (HHFA). This paper was noteworthy in that it demonstrated a remarkable increase in volatility of the chelates of the fluorinated ligands. This increase in volatility on fluorination, has been attributed to a reduction in van der Waals forces and a decrease in intermolecular hydrogen bonding (158).

Since 1963 inorganic gas chromatography has become an active research field with Sievers and his coworkers (10,44-47,51,55,66,111, 113,122,123,129-36,139,143,144,150,153-63,167,175,190,191) being the principle contributors.

The most extensively studied chelates have been H(TFA) complexes of berylium (21,44,45,55,127,130,131,133,134,136,143,154,155,156,174, 175,190,191) and chromium (2,21,22,44,45,51,55,59,60,77,127,128,132, 133,136,139,140,158,160,174,190). Berylium has been successfully determined in such widely varied samples as polluted air (134, 155) and moon rocks (44) at levels as low as 10^{-13} grams. This phenomenal success with berylium can be attributed to its extreme volatility. Studies utilizing the inert β-diketone complexes of chromium have also been very successfull with chromium being determined in blood (22,66) and urine (140) at

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[1] See APPENDIX for structure and nomenclature of ligands.

levels as low as 10^{-11} grams. Geometric isomers of $Cr(TFA)_3$ complexes have also been separated by gas chromatography (44, 51, 158, 160) as have various optical isomers (158, 160).

Since 1963 the range of chelates of the β-diketonates which have been chromatographed has grown rapidly. A complete listing of the metals which have presently been studied is presented in Figure 1.1. A single asterisk marks complexes which have been determined quantitatively. The complexes with two asterisks have been eluted without apparent evidence of decomposition, and those with three asterisks produced chromatographic peaks. but there is evidence of some decomposition. The superscript, a, denotes complexes which have been eluted as mixed-ligand complexes with DBSO, TBP and TBPO. A superscript, b, indicates mixed-ligand complexes of TBP and the superscript, c, refers to the complex $MoO_2(ACAC)_2$.

The complexes of the lanthanides that are volatile and stable are of considerable interest. This interest has existed since the beginning of inorganic gas chromatography when Lederer(86) suggested the possibility of separation of the lanthanides as H(ACAC) complexes. The hoped for separation was not achieved in spite of extensive study by various research groups (13, 15, 24, 42, 46, 48, 95, 113, 122, 124 146, 148, 151, 154, 159, 167, 180, 181). The primary outgrowth of this research was the discovery that the lanthanide complexes possessed a primary coordination number greater than 2n, where n is the charge on the metal ion. An excellent summary of these studies is presented in a review article on the coordination chemistry of the lanthanides (107). The majority of the tris-β-diketonates of the lanthanides are eight coordinate. After formation of the tris

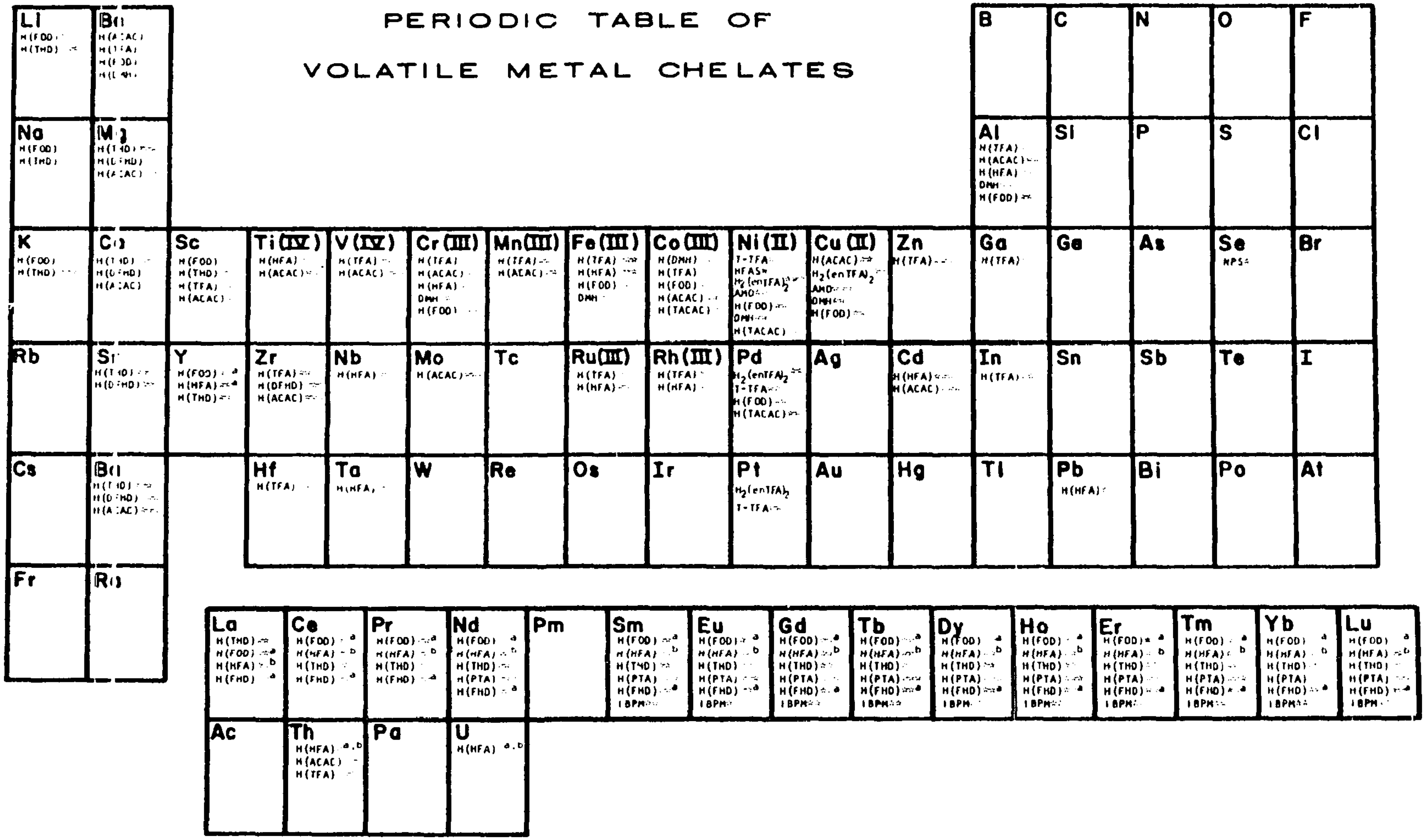


Figure 1.1. Periodic table showing metal chelates studied by gas-liquid chromatography
References: (2, 8, 10, 11, 12, 13, 14, 16, 17, 18, 19, 21, 22, 14, 15, 40, 41, 44, 45, 46, 47, 79, 51, 55, 57, 59, 60, 61, 66, 69, 77, 78, 105, 106, 109, 110, 111, 112, 113, 115, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 139, 140, 142, 143, 144, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 167, 168, 171, 172, 173, 174, 175, 176, 180, 181, 182, 190, 191, 192, 193)

complex with the β-diketone ligands, the remaining vacant coordination sites are filled with the solvent in which the lanthanide resides. When these sites are filled with water, problems occur in the thermal stability and in the solvent extraction of lanthanide β-diketonates. Mitchell (104) has shown that hydrated lanthanide β-diketonates decompose during thermal analysis. Apparently the presence of water in the coordination sphere contributes to the thermal instability by promoting self hydrolysis of the complex at elevated temperature (121). This thermal decomposition makes it impossible to determine the lanthanides by gas chromatography. Sievers and coworkers (46, 159) reasoned that the most promising approach in obtaining anhydrous, stable, volatile complexes would be the formation of complexes with ligands which were sufficiently bulky to offer steric interference to the formation of hydrates. With this goal in mind, they synthesized 2, 2, 6, 6-tetramethyl-3, 5-heptanedione, H(THD). Using H(THD) they were able to prepare solid, anhydrous chelates of the lanthanides and reported the first successful determination of the lanthanides by gas chromatography (46).

Springer, Meek and Sievers (167) synthesized the β-diketone 1, 1, 1, 2, 2, 3, 3-heptafluoro-7, 7-dimethyl-4, 6-octanedione, H(FOD) to increase the volatility and retain the steric interference required for the formation of anhydrous complexes. They prepared the solid lanthanide chelates as monohydrates and found them to be easily dehydrated under vacuum. These anhydrous chelates were successfully chromatographed and were much more volatile than the H(THD) chelates. No gas chromatographic separation or quantitative data were reported and lanthanum, cerium and praseodymium chelates were not eluted. As a result of these studies, Eisentraut and Sievers were granted two U.S.

patents for separation of the lanthanides by fractional sublimation (48) and in the gas phase (47). Since this work several other research groups have synthesized new ligands and reported varying degrees of success (13, 122, 146, 148, 152, 180, 181).

A similar ligand, 1, 1, 1-trifluoro-5, 5-dimethyl-2, 4-hexanedione, H(PTA), was synthesized by two Japanese research groups, Shigematsu et al. (146, 148) and Tanka et al. (171). Rare earth chelates were reported to be anhydrous and some separations were reported, but decomposition of several of the chelates was shown.

All of the work concerning the lanthanides discussed to this point requires direct synthesis of solid complexes, purification, dehydration and dissolution in suitable solvent prior to chromatographic analysis. Sweet and Parlett (170) found that the lanthanides were incompletely extracted with H(THD) but no attempt at gas chromatographing the extracted species was made. The difficulty in the solvent extraction of the lanthanides is a result of the hydrophilicity of the dihydrated complex. This hydrophilic nature precludes efficient transfer to the organic phase in an extraction. Ferraro and Healy (54) found that an organic base such as tri-n-butyl phosphate will displace water from the coordination sphere of the complex, thereby making the complex hydrophobic and effecting a quantitative extraction. The research on mixed-ligand extraction, commonly referred to as synergistic extraction, has been thoroughly reviewed by Carey (27) and Mitchell (104).

Mitchell (104) has recently completed a study of synergistic extraction systems, employing fluorinated β - diketones and various organic donors. Several mixed-ligand complexes which were both volatile and quantitatively extracted were identified. Mitchell has shown that the formation of a mixed-ligand complex of the lanthanides in an extraction is represented by Equation 1.1

$$M^{+3} + 3H(L)_o + nD_o \rightleftarrows M(L)_3 \cdot nD_o + 3H^{+} \qquad (1.1)$$

The subscripts (o) are used to indicate 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 dependent on the amount of neutral donor, D. The extraction becomes quantitative when the stoichiometric amount of neutral donor is added. Mitchell also reported that symmetrical, fully fluorinated ligands, containing seven carbon atoms or more, possessed the best extraction properties.

Butts and Banks (25) were the first to apply mixed-ligand systems to the extraction and subsequent gas chromatographic determination of the lanthanides. The technique allowed direct preparation of anhydrous HFA-TBP chelates in the organic phase ready for injection into the gas chromatograph. Sieck(151) has studied several mixed-ligand systems and achieved successful elution of the lanthanides as mixed-ligand complexes. Although the chelates of the lanthanides were chromatographed, separations were not achieved and quantitative results were not reported. Sieck et al. (152) have reported the successful separation and quantitative determination of uranium and thorium as the HFA-DBSO mixed-chelates. Mitchell and Banks (105) have shown both $U(HFA)_4$ and $UO_2(HFA)_2 \cdot TBP$ to be volatile and chromatographable. The use of solvent extraction in combination with gas chromatography allows coupling of the specificity of solvent extraction techniques with the resolution capabilities of gas chromatography to achieve useful analytical methods.

As shown in Figure 1. 1, many metals have been eluted as complexes with β-diketones but have shown signs of apparent decomposition. Apparently this decomposition is caused by the labile nature of the complexes. To form more stable complexes Bayer et al. (9, 10) synthesized the ligand 1, 1, 1, 5, 5, 5-hexafluoro-2-hydroxylpent-2-en-4-thione, H(THFA) and successfully chromatographed the bis complexes of nickel, palladium and platinum. Belcher et al.(17) reasoned that complexes of the a-b type (1), that is those preferring both first and second row donor atoms, might form complexes of high stability with sulfur donor ligands. To demonstrate this point Belcher and coworkers (17, 18, 19) synthesized 1, 1, 1-trifluoro-2-hydroxylpent-2-en-4-thione, H(TTFA) and have reported separation of nickel, palladium and platinum and quantitative analysis for nickel. Belcher et al. (16) also have reported several new ligands which are quadridentate derivatives of acetylacetoneethylenedi-imine. Only limited gas chromatographic success has been demonstrated with complexes of these ligands. Miyazaki et al. (106) have prepared nickel chelates of some β-diketo-amine derivatives of H(ACAC) and salicylaldehyde, some of which are reported to be thermally stable. Richards and Sievers (123) reported the synthesis of bis(hexafluoroacetylacetone) ethylenedi-imine and its copper complex but did not report any gas chromatographic studies. Although limited in its success, this approach to chelate formation may prove to be exciting in the future.

C. Gas chromatographic Columns

The most important, the most studied and perhaps the least understood element of gas chromatography is the column. The column effects the actual separation of the sample components and is the most widely varied parameter in gas chromatography. Columns can be characterized into four types based on their contents and mode of interaction. The first type and most frequently used is the gas-liquid column in which an open tube of up to 15 feet in length and typically 1/4" o.d. is packed with a solid support of some relatively inert material. The solid material has been coated with an immobile liquid prior to packing. With this type of column, partitioning occurs primarily between the sample and the immobile liquid. The second type is the gas-solid column. The solid support is packed in a column without prior coating and the partitioning occurs between the sample and the solid support itself. The third type is the capillary or open tubular column. A long (up to 1000 meters) tube of small inside diameter (0.15 to 75 mm) is coated with a thin film of immobile liquid (50). The partitioning occurs between the liquid phase and the sample. The last type is the packed tubular column. The long tube used for open tubular columns is packed with a solid support which has been coated with a liquid phase. The partitioning process again occurs primarily between the liquid phase and the sample. The majority of gas chromatographic studies have been performed on columns of the gas-liquid type, including those reported herein; further discussion will therefore be limited to this type of columns.

The gas-liquid chromatographic column may be considered as a liquid phase evenly loaded on a finely dispersed solid support which is packed into a column. This arrangement provides a large liquid phase surface area which is in contact with the mobile phase or carrier gas. The sample components are carried through the column by the mobile phase and are partitioned with the liquid phase. The basic theory of this type of partitioning has been described by Giddings (63). His description stresses the partitioning of solute between mobile phase and liquid stationary phase as the predominant mechanism and neglects other partitioning phenomena. It may be valid to neglect other contributions to the retention volume in most (but certainly not all) practical gas-liquid phase and liquid-liquid chromatographic systems (31). Perhaps more than is generally recognized, the solute may also be retained in the column by adsorption (i) at the gas-liquid interface (or liquid-liquid interface in liquid-liquid chromatography) and/or (ii) as a result of the presence of the solid support. Martin (96) has shown that serious errors have been made by neglecting the possibilities of other interactions, in particular adsorption on the gas-liquid interface. Waksmundzki (185) has suggested 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 from the liquid solution by the support surface, c. adsorption of solute molecules on the surface of the liquid phase, d. adsorption of solute molecules from the gas phase by the bare surface of the support, and e. change in composition of the liquid phase by adsorption of its components. Since a great deal of non-ideal interaction has been reported in the gas chromatography of metal complexes (113, 128, 132, 136, 135, 151, 177, 183) each of these five phenomena will be discussed in some detail.

1. Partitioning of molecules between the gas and liquid phase

The basic equation for partitioning in gas-liquid chromatography has been developed through an extension of distribution theory for solute distribution between two phases in equilibrium and can be written, (3,76)

$$V_{Rg}{}^{\circ} = K_s V_L \tag{1.2}$$

where $V_{Rg}{}^{\circ}$ is the retention volume per gram of packing, K_s is the partitioning coefficient for the solute in the liquid phase, and V_L is the volume of the liquid phase per gram of packing. Equation (1.2) assumes that, (a) the gas phase is incompressible, (b) that there is equilibrium distribution of solute molecules between phases and (c) that there is no adsorption of solute by the solid support or the liquid phase. The indiscriminate use of assumption (c) has lead to several errors in interpretation of chromatographic results (96), particularly in the calculation of activity coefficients.

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

Equation (1.2) is useful in describing chromatographic behavior for the majority of applications, predicting linear increase in K_s with an increase in liquid phase. The equation does not account for observed changes in elution order with ratio of liquid phase to solid support (43,58,98).

To elucidate such phenomena Martin (96) proposed that adsorption on the liquid-gas interface was occurring. A new equation for retention volume was formulated which accounted for this adsorption. Assuming the contribution to the retention volume from adsorption on the liquid surface is proportional to the surface area of the liquid, Equation 1.2 can be extended as follows.

$$V_{Rg}{}^{\circ} = K_s V_L + k_a A_L \qquad (1.3)$$

Where A_L is the surface area of liquid per gram of packing, k_a is a proportionality constant which depends on the tendency for the solute to adsorb on the particular liquid surface, with units of centimeters when $V_{Rg}{}^{\circ}$ is in cc/g and A_L is in cm^2/g. Martin found Equation 1.3 adequately described the retention behavior of n-hexane on Chromosorb P and Chromosorb W columns containing varying percentages of β, β' thiodipropionitrile. This type of adsorption was later found to follow adsorption described by the Gibbs adsorption equation (97). Martin's findings were confirmed and extended by Pecsok, et al., (117) and directly substantiated by the static measurements of Martire, Pecsok and Purnell (100).

In each case a polar stationary phase was used, following Martin's suggestion that an appreciable Gibbs adsorption effect would only be observed with such phases. Later (101) this statement was generalized to include any system in which the solute activity coefficient exceeded about five. Martire has shown this condition to be sufficient but also demonstrated that liquid surface effects may be observed in certain polar solute-polar solvent systems in which the solute activity coefficients are only around unity (99). He further demonstrated that two types of adsorption at the gas-liquid interface may occur. The first type is characterized by large solute activity coefficients, i.e., the bulk liquid is a poor solvent. In this situation the less polar the solute is with respect to the solvent and the less soluble it is in the bulk liquid, the larger the adsorption effect. The second type is characterized by low solute activity coefficients, significant solute solubility in the bulk liquid and a solute and solvent molecules of comparable high polarity. When these conditions are met the solute is preferentially adsorbed because of strong bonding between the solute and liquid surface.

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

Of all the contributions to the retention volume, this interaction is the most frequently ignored. For this interaction to occur the solute molecules must diffuse through the liquid phase to the support material. It may be argued that at high loads the solute has insufficient time to diffuse through the liquid to the solid support where it may be adsorbed. Keller (80) treating diffusion as a random walk, reported rough calculations for the time required for a molecule to reach the solid surface of a 30% loaded column. His value of 7.6×10^{-3} seconds is certainly fast enough under most conditions of GLC for a molecule of solute to reach the support surface. As of yet no experimental evidence has been conclusively reported to substantiate this interaction. This lack of evidence is probably a result of the difficulty in physical measurement. In any event, when completely considering retention behavior this phenomena must be considered in the sense that in all situations the solute molecule can reach the support surface.

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

Solid supports for the stationary phase have long been known to interact with some types of solutes (31). Keller (79, 80) has proposed an equation for the retention volume of a solute in near equilibrium distribution with three phases. This equation is an extension of Equation 1.2

$$V_{Rg}^{\circ} = KV_L + k_s A_s \qquad (1.4)$$

where V_{Rg}°, K and V_L are as previously defined, A_s is the area of the bare support surface, k_s is the ratio of the concentration of solute adsorbed by the solid support to the solute in the gas phase. It appears that at high levels of liquid loading the area of the bare support, A_s, will approach zero and the equation will reduce to the simple form of Equation 1.2. However, adsorption at the liquid-solid interface when solute and solvent compete for the support surface should also be considered (64). The existence of this type of interaction has been conclusively demonstrated by Urone *et al.* (179) for the system of acetone-tri-o-tolyl-phosphate on Chromosorb P and W. When the surface is completely covered, all apparent support effects must stem from this type of adsorption. At less than monolayer coverage, or if the solvent does not wet the support, adsorption can occur at both the liquid-solid and exposed interfaces.

The characteristics of solid adsorption are completely different from liquid adsorption (117). Besides an increase in retention time, the irreversible adsorption on the solid support causes bad tailing and no reproducibility. When solid adsorption occurs the retention volume extrapolates to the retention volume observed on the bare solid. With liquid surface adsorption, the extrapolated value differs from the observed value on bare support.

5. Change of composition and character of the liquid phase caused by adsorption of its components

As discussed above, adsorption to the solid support surfaces has been reported, even with liquid loadings as high as 20%. Craig (32) contends that the solid support interaction at such high loadings is unlikely, pointing out that the surface of the solid support is completely covered at around 2% liquid loading. He has suggested the possibility of orientation of the liquid phase molecules as they are laid down on the support. This ordering would change the structure of the phase at the monolayer and possibly second layer level.

To a certain extent the experimental work of Urone _et al._ (179) and Waksmundzki (185) have offered support to confirm Craig's hypothesis. Both reported minima in retention volume at low percentage liquid phases and maxima at about 2% liquid phase loading. They attributed these observations to adsorption on the monolayer of the liquid surface at 0.6% liquid phase and to adsorption on a strongly oriented second layer at 2% liquid phase. Other workers (116, 58, 35) have reported chromatographic effects dealing with alteration of liquid phase properties by the solid support particularly when chromatographing strongly polar solute using non-polar liquid phases. This evidence suggests the existence of retention effects arising from solute interaction with highly oriented layers of the liquid phase on the solid support and not interaction at the liquid-solid interface as Keller (80) suggested. In terms of actual contribution to retention volume, both effects would have the same result, and precisely which effect is occurring is somewhat difficult to assess In both situations the phenomena must certainly be dependent on the volume of the liquid phase, V_o and proportional to the concentration of solute in the gas phase, k_o. Because of this correlation another term,

k_oV_o, must be added to the retention volume equation to account for the contribution of solute interaction with the liquid phase either at the solid-liquid interface or at highly oriented layers.

By including all terms contributing to the retention of a solute on a GLC column, the resultant general equation would appear as follows:

$$V_{Rg}^{\circ} = KV_L + k_aA_L + k_sA_s + k_oV_o \tag{1.5}$$

where KV_L represents the contribution to retention from partitioning of the solute between the gas and the liquid phase, k_aA_L represents the contribution to retention from adsorption of the solute on the surface of the liquid phase, k_sA_s represents the contribution to retention from adsorption of the solute on the bare support and k_oV_o represents the contribution of solute interaction with the liquid phase either at the solid liquid interface or at highly oriented layers or both.

It is immediately obvious that the partitioning observed in a gas chromatographic column is more complicated than Equation 1.2 suggests. Which terms are important in determining the retention volume for a solute will depend upon the experimental situation. By judicious selection of conditions and experiments, the predominate terms for a given system can be determined.

Except for special experimental conditions, the contribution to retention of solute due to interaction at the liquid-solid interface or at a few highly oriented liquid phase layers, k_oV_o, can be considered negligible (178, 179). The general retention Equation 1.5 then reduces to the following,

$$V_{Rg}^{\circ} = KV_L + k_sA_s + k_aA_L \tag{1.6}$$

The several retention mechanisms can be treated as essentially independent if sufficient solvent is present on the solid support to act as a bulk liquid with a depth greater than that of the gas-liquid and liquid-solid interficial layers (31). The precise depth has not been defined in this context because the definition of a surface layer is arbitrary. The surface layer can be considered to be the distance from the surface to the point to which the influence of the surface extends (67, 80, 99). Conder and coworkers (31) stress that even at liquid phase loadings of 10% the film thickness is insufficient to be considered a true bulk solvent and warn that interficial effects are meaningless in the absence of the required reference state bulk liquid. If one works at very small sample sizes, ideally at infinite dilution, the absence of a true bulk solution as a reference state is minimized. Commonly (20, 84, 96, 97, 99, 100, 101, 117, 118, 169) the initial experimental approach is to assume infinite dilution and that no contribution to retention volume occurs from the adsorption to the solid support. In this case Equation 1.3 holds. By varying liquid phase loadings at a constant temperature, a plot of $V_{Rg}°/A_L$ versus V_L/A_L can be used to evaluate K and k_a.

This procedure is of no use if solid support effects occur and cannot be applied at all unless A_L is known as a function of V_L. It is extremely difficult to obtain values for A_L that are not values for gross surface area, solid support plus liquid surface (31).

A preferable procedure, which avoids both of these shortcomings, is to plot $V_{Rg}°/V_L$ against $1/V_L$. This allows K to be obtained whether A_L is known or not and if A_L is known both K and k_sA_s can be obtained from the plot as described by Conder (30).

Conder (30) further contends that retention measurements at the peak maxima are unreliable in cases when asymmetrical peaks appear. Recently (84) it has been demonstrated that a modification of this method can be applied to solution dominated asymmetrical peaks, i.e., those at greater than infinite dilution. The observation of peak asymmetry implies that sample sizes are so large that the condition of effective infinite dilution is not achieved for one or more of the distribution mechanisms contributing to the retention. It is also possible that asymmetry observed is merely an artifact of the injection or detection system (183). Peak asymmetry suggests which mechanisms are affecting the retention. The major factors determining the peak profile are threefold: (a) the form of the distribution isotherm for each retention mechanism, (b) a change in flow rate across the two boundaries making up the peak, caused by flux of solute between stationary and mobile phases (sorption effect), and (c) kinetic band broadening processes such as diffusion and slow mass transfer (non-ideality) (30).

Combinations of these three factors frequently give rise to asymmetrical peaks, one side being "self-sharpening" with a very steep slope and the other being "diffuse." The direction and extent of asymmetry is measured by the skew ratio, η, defined as the slope of the trailing boundary of the peak divided by that of the front boundary, at the points of inflection (33). Non-ideality tends to reduce the slope of both boundaries so that η is determined primarily by effects (a) and (b). The sorption effect, (b), invariably skews the peak in the direction of $\eta > 1$. In contrast, isotherms for distribution of solute between the gas phase and an adsorbed liquid surface phase are generally of Langmuir curvature giving $n < 1$. Adsorption on, or induced by a solid surface, such as that of the support, can be associated with isotherm curvature in either sense, but most commonly in the Langmuir sense which gives $n < 1$.

The contribution to retention volume by adsorption at the solid surface can easily be determined by a plot of partition ratio, $\underline{k}$. as a function of grams of liquid phase, providing constant column lengths, flow velocities and temperatures are maintained (183). When adsorption occurs a non-zero intercept is found, the $\underline{k}$ value of the intercept, representing the adsorption on the solid surface.

The partitioning of metal chelates on GLC columns has been studied by several workers (151). They have reported the retention volume, $V_{Rg}°$, 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. Uden and Jenkins (177) and Sieck (151) have reported some unusual adsorption and displacement effects in the determination of metal β-diketonates by GLC. It has been suggested that these effects are caused by interaction with the solid surface; however, precise experimental evidence was not presented to support this conclusion and the exact nature of this interaction is not known.

D. Lanthanide Paramagnetic Shift Reagents

Nuclear magnetic resonance, nmr, spectroscopy is one of the most powerful tools available to the chemist for the elucidation of structure. Before coupling constants, chemical shifts and proton ratios can be easily measured, the peaks of a nmr spectrum must be clearly separated. When a molecule becomes complex, the overlap of proton resonances becomes a serious problem and the information obtainable from the nmr spectrum is severely restricted. The use of various techniques such as solvent shifts, spin decoupling or INDOR experiments, deuterium substitution, derivatisation and the use of higher frequency spectrometers (26) may offer some help in resolving higher order spectra but these techniques are time consuming or require expensive sophisticated instrumentation.

Paramagnetic complexes such as the acetylacetonates of nickel (II) and cobalt (II) have long been known to increase chemical shift differences (71). Unfortunately, the chemical shifts realized are small and the relaxation times of the metals long, resulting in broadened and little improved spectra.

In 1969 Hinckley (70) reported the use of the dipyridine adduct of tris (2,2,6,6-tetramethyl-3,5-heptanedianato) europium (III), $Eu(THD)_3 \cdot 2py$, to induce chemical shifts in cholesterol monohydrate. He found relatively large chemical shifts were produced to lower field without serious line broadening. Sanders and Williams (137) subsequently reported that increased effectiveness was realized by using the $Eu(THD)_3$ complex without pyridine. Sanders also reported that the $Eu(THD)_3$ shift reagent was of limited utility when used with weak Lewis bases. Demarco et al. (36) reported that the solubility of the THD chelates was relatively low in non-alcoholic solutions. This low solubility prevented the obtaining of maximum shifts by limiting the concentrations of THD chelates in the solution. In spite of these problems, the analogous complexes of praesodymium (22), neodymium, samarium, terbium, dysprosium and holmium (34) were investigated and found to induce shifts to higher field; whereas, the ytterbium, erbium (34) and thulium (5) complexes induce shifts to lower field. The majority of the complexes, excluding samarium and neodynium, induced shifts of greater magnitude than europium, but the line broadening was extensive.

Rondeau and Sievers (126) recently described the application of $Eu(FOD)_3$ and $Pr(FOD)_3$ complexes as shift reagents. These reagents possessed increased Lewis acidity as a result of the replacement of hydrogen by fluorine in the ligand shell and were reported to be extremely soluble. Because of the increased solubility and Lewis acidity, the shifts obtained were superior to those obtained with the THD complexes. Some spectral interference from the t-butyl protons of H(FOD) was observed and to obtain maximum shifts it was necessary to dehydrate the FOD complexes in a vacuum desiccator over P_4O_{10}.

Sanders and Williams (138) reported the development of an optically active shift reagent. This europium reagent, derived from d-camphor, was shown to be useful in the resolution of (R)-and (S)-substrates of α-phenylethylamine.

II. PURPOSE

It is the purpose of this study to develop an analytical method for the quantitative separation and determination of the lanthanides by gas chromatography. Two mixed-ligand systems will be evaluated in terms of their thermal stability and gas chromatographability to determine the most suitable gas chromatographic system for the determination of the lanthanides. Various columns will be studied in regard to partitioning, separation efficiency and non-ideal behavior.

The utility of the electron capture detector for the determination of the lanthanides as mixed-ligand complexes will be determined and an investigation into the use of lanthanide complexes as paramagnetic shift reagents will be made.

It is hoped that these studies will contribute to the growth and applicability of gas chromatography as a technique for the analysis of inorganic species.

III. AN INVESTIGATION OF GAS CHROMATOGRAPHIC SYSTEMS USED IN DETERMINATION OF MIXED-LIGAND COMPLEXES

A. Introduction

This work will describe a study of the various parameters which are incorporated into a gas chromatographic system for the determination of mixed-ligand complexes of the lanthanides. A gas chromatographic system is defined as the combination of the chemical system in which the species to be determined exists and the instrumental system by which the species will be determined. Sieck (151) reported success in chromatographing several mixed-ligand systems, but he was unable to achieve practical separations and no quantitative work was reported.

To be of value as an analytical technique, rapid and quantitative separations must be achieved. Several mixed-ligand systems will be evaluated in terms of thermal stability, retention time and column performance. Columns of varying length and liquid phase will be evaluated. The optimum chromatographic system will be thoroughly investigated and a method for the separation and quantitative determination of the lanthanides developed. A study of selected interferences will also be presented.

B. Experimental

1. Apparatus

a. Gas chromatograph A Hewlett-Packard Model 5756B gas chromatograph equipped with an on column inlet, flash vaporization inlet, thermal conductivity detector, dual hydrogen flame ionization detector and ^{63}Ni electron capture detector, was used for all studies.

The majority of the chromatograms were recorded with a Hewlett-Packard Model 7128A recorder. All quantitative data were obtained from chromatograms recorded with a Bristol Model 560 Dynamaster recorder equipped with a Disc-Integrator.

b. Spectrophotometers Infrared spectra were obtained using a Beckman IR-7 infrared spectrophotometer.

c. Spectrometers A Hitachi-Perkin Elmer R-20B nuclear magnetic spectrometer was used for all ^1H nmr spectra. The ^{19}F nmr spectra were obtained from a modified Varian HA 100 nuclear magnetic spectrometer.

d. Thermogravimetric analyzer All thermogravimetric analyses were performed on a DuPont Model 950 Thermogravimetric Analyzer.

e. pH meter A Corning pH meter Model 12 equipped with a fiber type calomel electrode, Beckman Catalogue No. 1170 and a glass electrode, Beckman Catalogue No. 1190-42, was used for all pH measurements.

f. Automatic shaker The solvent extraction mixtures were all agitated by a Burrell Wrist-Action Shaker.

2. Reagents and materials

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

b. Cations Solutions of copper(II), aluminum(III), calcium(II), iron(III), uranium(VI), zinc(II) and thorium(IV) were prepared from Fischer Certified Reagent copper (99.999%) and aluminum chloride; Baker Analyzed calcium chloride and ferric chloride; Mallincrodt uranyl acetate dihydrate; Fischer Scientific thorium nitrate and Hill electrolytic zinc (99.99%).

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

The β-diketone 1, 1, 1, 2, 2, 6, 6, 7, 7, 7-decafluoro-3, 5-heptanedione, H(FHD), wassynthesizedin this laboratory from Pierce Chemicals ethyl penta-fluoro propionate and perfluoropropionaldehyde methyl hemiacetal by a procedure modified from that of Springer, Meek and Sievers (167). The details of this procedure will be given in the section below on 1, 1, 1, 2, 2, 6, 6, 7, 7, 7-decafluoro-3, 5-heptanedione.

d. Neutral donors Di-*n*- butylsufoxide, DBSO, was obtained from Crown Zellerbach and purified by recrystalization from petroleum ether. Tri-*n*-butylphosphate, TBP, was obtained from Fischer Scientific Co. and purified by the procedure of Irving and Edgington (72).

e. Solid supports Chromosorb W-HP was used in all studies and was obtained from Applied Science Laboratories.

f. Liquid phases All liquid phases were obtained from Analabs Inc.

g. Columns Stainless steel columns were prepared from laboratory stock stainless steel tubing. Glass columns were prepared from Pyrex, borosilicate glass tubing.

h. Solvents All solvents were reagent grade.

3. Techniques

a. Preparation of stock solutions of cations Solutions of aluminum (III) and calcium(II) were prepared by dissolving the metal chloride in dilute hydrochloric acid, evaporating to near dryness and diluting to standard volume with sodium acetate-acetic acid, pH=5.5, buffer.

Solutions of iron(III) were prepared by dissolving the metal chloride in deionized water and diluting to volume with 0.1 M nitric acid to prevent precipitation of the ferric hydroxide. Stock solutions of the lanthanides, except cerium, were prepared by dissolving the 99.9% oxide in dilute hydrochloric acid , evaporating to near dryness and diluting to volume with pH=5.5 acetate buffer. To prepare solutions of cerium from the oxide it was necessary to add one drop of fluosilicic acid to the heated dilute hydrochloric acid. After dissolution, the sample was treated in a manner identical with that of the other lanthanides. Solutions of uranyl were prepared by dissolving uranyl acetate in deionized water and diluting to volume with pH=5.5 buffer. Thorium chloride solutions were prepared by passing aqueous thorium nitrate through a Dowex 1 x 8 ion exchange column in the chloride form. Standard solutions of zinc and copper were prepared by weighing the appropriate amount of electrolytic zinc (99.99%) and copper (99.999%), dissolving in hydrochloric acid and evaporating to near dryness. After evaporation the samples were diluted to volume with deionized water.

b. Preparation of buffer solution Approximately 27 grams of sodium acetate trihydrate was weighed into a one-liter bottle and dissolved in one liter of deionized water. The pH was adjusted to 5.5 by the addition of hydrochloric acid.

c. Preparation of stock ligand solutions Solutions of neutral donors and H(FHD) were prepared by weighing the pure reagents into a volumetric flask and diluting to volume with redistilled cyclohexane.

d. Solvent extraction procedure The technique employed for the solvent extraction of the lanthanides as mixed-ligand complexes was similar to that used by Sieck (151). The solvent extractions were performed in 15 ml screw cap glass test tubes. The inside lining of the screw caps were replaced with a Teflon disk to prevent any interaction with the plastic top. The samples were prepared by contacting 1.00 ml of the aqueous solution with 1.00 ml of cyclohexane containing β-diketone in an amount four times the total metal concentration and neutral donor in an amount three times the total metal concentration. Shaking times of 30 minutes were used to establish equilibrium. After equilibrium was established, the samples were washed with 1.0 N sodium hydroxide to remove excess H(FHD).

e. Sample injection All samples were taken directly from the organic phase of the extractions and injected into the chromatograph with Hamilton microsyringes.

f. Preparation of column packing An adaptation of the method described by Butts (24) was used to prepare column packings. Five grams of dry support is placed in a 2 inch x 10 inch cylindrical tube fitted with a glass frit. A solution of the liquid phase in 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. Filtered air is then passed through the packing while heat is applied by infrared lamps. The solvent is thereby removed leaving dry, uniformily coated support.

g. Packing and conditioning of columns All columns were washed with methylene chloride, acetone and ethanol and air dried before packing. The dried packing, as prepared above, was then poured into the columns and compacted by agitation from a Burgess

Vibro-graver. The column ends were plugged with glass wool.

All columns, with the exception of the Dexsil 300 GC columns, were conditioned at 50° C below the maximum operating temperature for the particular liquid phase for one hour without flow and then three to five hours with a helium flow of 50 ml/min. The Dexsil 300 GC columns were conditioned for one hour at 250°C without flow; then the temperature was programed to 350°C at 4°C/min.

4. Analytical determinations

a. Titrations of cations The stock solutions of the lanthanides and yttrium were standardized by titration with EDTA using Xylenol Orange as indicator (81). Solutions of aluminum, calcium and iron were determined by titration with EDTA using NAS indicator as described by Fritz *et al.* (56). The EDTA was standardized with zinc. The uranyl stock solutions were standardized by titration with EDTA using PAN indicator, as described by Lassner and Scharf (83). The thorium solutions were standardized by titration with EDTA using Xylenol Orange as indicator (181).

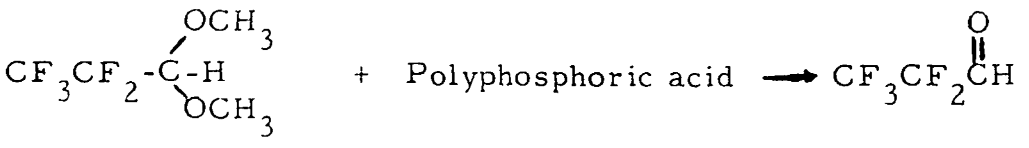
C. Results and Discussion

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

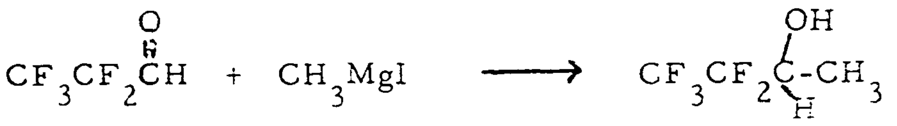
Several criteria must be met for the formation of a chemical system which is suitable for the gas chromatographic determination of metals. The metal must be rendered volatile and thermally stable under normal gas chromatographic conditions. Normal gas chromatographic conditions are defined as the use of temperatures of ambient to 300°C and common materials such as glass or stainless steel for column tubing. The formation of volatile metal species must be performed in a reasonable amount of time and be quantitative. The volatile metal species must be soluble in a suitable solvent for sampling by syringe prior to gas chromatographic determination and the retention time of the volatile metal species in the chromatographic column must be relatively short, that is 30 minutes or less.

Metal chelates with fluorinated β-diketones have been shown to be extremely volatile. The application of these chelates has been disscussed in detail in Section I, LITERATURE REVIEW AND THEORY. Mitchell (104) has recently demonstrated the feasibility of the formation of various mixed-ligand complexes of the lanthanides by solvent extraction. Butts (24) and Sieck (151) have demonstrated success in the gas chromatography of a number of these mixed-ligand systems. By combining solvent extraction with gas chromatography, several advantages are realized. The extraction system adds selectivity to the rapid quantitative formation of volatile species directly in the organic phase. This selectivity is then combined with the sensitivity and resolving power of gas chromatography.

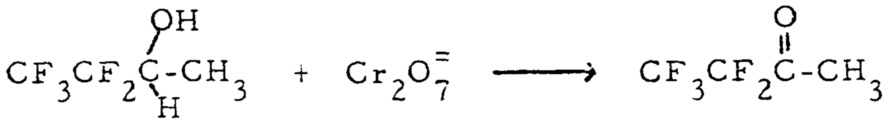
At the completion of his studies, Mitchell (104), suggested that the ligand 1, 1, 1, 2, 2, 6, 6, 7, 7, 7-decafluoro-3, 5-heptanedione would possess the optimum properties for extraction of the lanthanides as mixed-ligand complexes while forming an extracted species volatile enough for gas chromatographic analysis. To prepare this ligand the following synthetic route was proposed by John J. Richard, Ames Laboratory.



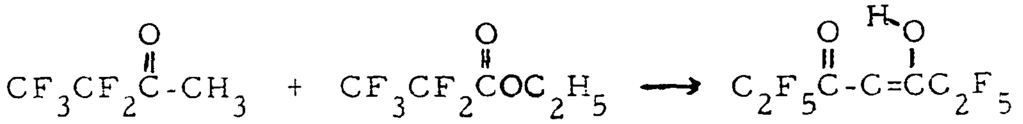
$$CF_3CF_2\text{-}\overset{\diagup OCH_3}{\underset{\diagdown OCH_3}{C}}\text{-}H + \text{Polyphosphoric acid} \longrightarrow CF_3CF_2\overset{\overset{O}{\|}}{C}H \qquad (3.1)$$



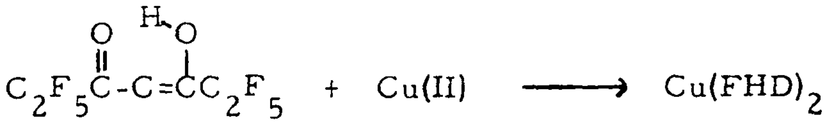
$$CF_3CF_2\overset{O}{\overset{\|}{C}}H + CH_3MgI \longrightarrow CF_3CF_2\underset{H}{\overset{OH}{C}}\text{-}CH_3 \qquad (3.2)$$



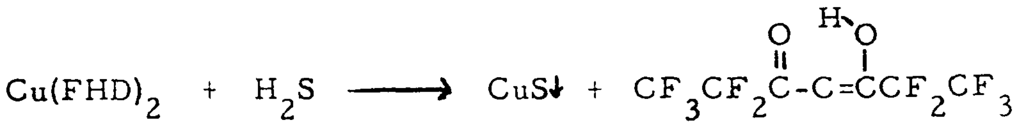
$$CF_3CF_2\underset{H}{\overset{OH}{C}}\text{-}CH_3 + Cr_2O_7^{=} \longrightarrow CF_3CF_2\overset{O}{\overset{\|}{C}}\text{-}CH_3 \qquad (3.3)$$



$$CF_3CF_2\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CF_3CF_2\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow C_2F_5\overset{O}{\overset{\|}{C}}\text{-}C{=}\overset{H\text{-}O}{\overset{|}{C}}C_2F_5 \qquad (3.4)$$



$$C_2F_5\overset{O}{\overset{\|}{C}}\text{-}C{=}\overset{H\text{-}O}{\overset{|}{C}}C_2F_5 + Cu(II) \longrightarrow Cu(FHD)_2 \qquad (3.5)$$



$$Cu(FHD)_2 + H_2S \longrightarrow CuS\downarrow + CF_3CF_2\overset{O}{\overset{\|}{C}}\text{-}C{=}\overset{H\text{-}O}{\overset{|}{C}}CF_2CF_3 \qquad (3.6)$$

This synthetic route constitutes a modification of that used by Springer, Meek and Sievers (167) for the synthesis of other fluorinated β-diketones and is presented in detail below.

The Grignard reagent (CH_3MgI) was prepared by adding 20 g magnesium (0.8 Mole) to 300 ml of absolute anhydrous ethyl ether (Baker), in a three-necked, round-bottom , one-liter flask. The flask was fitted with a water cooled reflux condenser, a motor driven propeller stirrer and a 100 ml addition flask. 114 g (0.8 Mole), of methyl iodide was placed in the addition flask and then added dropwise to the magnesium-ether mixture with constant stirring. A slow reflux was maintained by heating the mixture with a heating mantle during the addition of methyl iodide. After all the methyl iodide was added reflux was maintained for one hour. The resultant reagent was allowed to cool over night.

The addition funnel was removed from the three-necked, round-bottom flask containing the Grignard reagent and replaced with a 0.25 inch gas delivery tube. The water reflux condenser was replaced with a dry ice acetone cold finger. The other end of the gas delivery tube was fitted to a 500 ml round-bottom flask containing 100 ml of polyphosphoric acid. A thermometer and 100 ml addition flask were fitted to the flask. The polyphosphoric acid was heated with stirring to 150-180°C. 100 g of perfluoropropionaldehyde methyl hemiacetal was placed into the addition flask and added dropwise over a five hour period. The resultant perfluoropropionaldehyde was vaporized and delivered to the Grignard mixture via the gas delivery tube and mixed with constant stirring. After addition was complete the gas delivery tube was replaced with a glass stopper and the reaction mixture in the one-liter flask was refluxed for 45 minutes. The mixture was then cooled and hydrolyzed by pouring over cracked ice and acidifying with 10% sulfuric acid. The resultant solution was extracted four times with ether. The ether extracts were then dried over night over calcium chloride.

The alcohol was then distilled, the fraction boiling between 70 and 83°C was collected, with a yield of 91%. The alcohol was thereafter added to 150 ml of glacial acetic acid in a three-necked, round-bottom, one-liter flask. The flask was fitted with a water cooled condenser, the stirrer and the addition flask. Sodium dichromate was prepared by dissolving 150 g of sodium dichromate in 104 ml of sulfuric acid and 250 ml of water. The dichromate solution was placed in the addition flask and added dropwise over a one-half hour period, with rapid stirring. The mixture was allowed to cool over night.

The desired ketone was rectified from the mixture, the fraction boiling between 38°-39°C was collected and dried over sodium sulfate, yield was 48%.

A two-liter, three-necked, round bottom flask was dried and fitted with a stirrer, water reflux condenser and addition flask. 150 ml of absolute ether (Baker) and 12 g (0.22 Mole) of sodium methoxide was added. 42 g (0.22 Mole) of ethyl perfluoropropionate was placed in the addition flask and added dropwise to the stirred mixture over a period of 40 minutes, and a cream colored solution resulted. 0.22 Mole of the ketone were diluted with 50 ml of absolute ether and placed in the addition flask. The ketone was then added dropwise over a period of one hour. The mixture was allowed to stir for two hours and then refluxed for one-half hour. After refluxing 100 ml of 2 M sulfuric acid was added. The ether layer was collected and the aqueous layer was extracted three times with ether. The resulting ether layer was then dried over molecular sieve. At this point and attempt was made at the distillation of the pure H(FHD). The ligand proved to be exceedingly hygroscopic and formed white crystals throughout the distillation apparatus on heating. To avoid this problem the following procedure was incorporated.

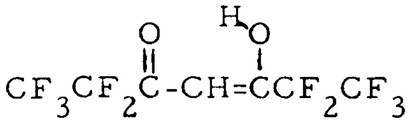
The combined ether extracts were washed with a saturated aqueous solution of copper(II) acetate. The green $Cu(FHD)_2$ complex was formed and extracted into the ether layer. The ether layer was placed in an evaporating dish and evaporated to dryness. The dried, green solid was then dissolved in absolute ether. Hydrogen sulfide was then bubbled through the solution resulting in the precipitation of copper sulfide and release of H(FHD). The solution was filtered and the pure ligand 1, 1, 1, 2, 2, 6, 6, 7, 7, 7-decafluoro-3, 5-heptanedione was distilled, the fraction boiling at 97 -98°C was collected, yield 42 %.

Elemental analysis was performed on the H(FHD) as prepared above and is reported in Table 3.1.

Table 3.1. Carbon and hydrogen analysis of H(FHD)

Compound	% Carbon		% Hydrogen	
	Calcd.	Found	Calcd.	Found
$C_7H_2F_{10}O_2$	27.27	27.33	0.66	0.64

The structure of H(FHD) was proven by infrared analysis, ^1H nmr and ^{19}F nmr to be:



$$CF_3CF_2\overset{\overset{O}{\|}}{C}\text{-}CH{=}\overset{\overset{HO}{|}}{C}CF_2CF_3$$

The infrared spectrum for H(FHD), neat, is shown in Figure 3.1. The band assignments are given in Table 3.2 and are in good agreement with those reported in the literature for fluorinated β-diketones (111, 114, 119, 124, 125, 164).

The ^1H nmr spectrum of H(FHD) is shown in Figure 3.2. The chemical shift assignments are given in Table 3.2 and are in good agreement with those reported in the literature for fluorinated β-diketones (111, 114, 164, 167). The small triplet and quartet at approximately

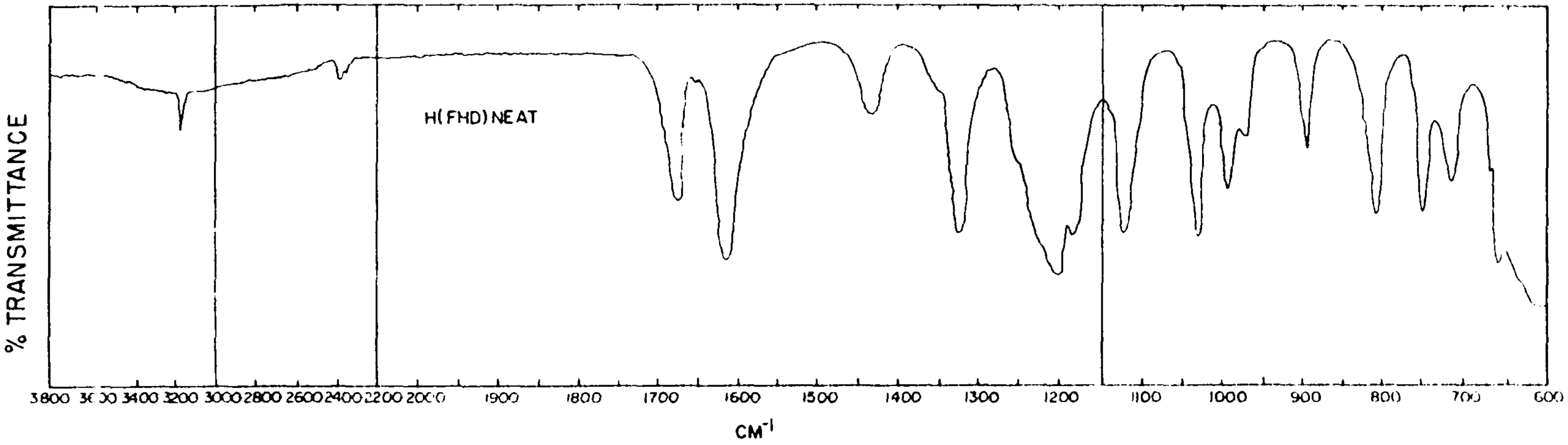


Figure 3.1. Infrared spectrum of H(FHD)

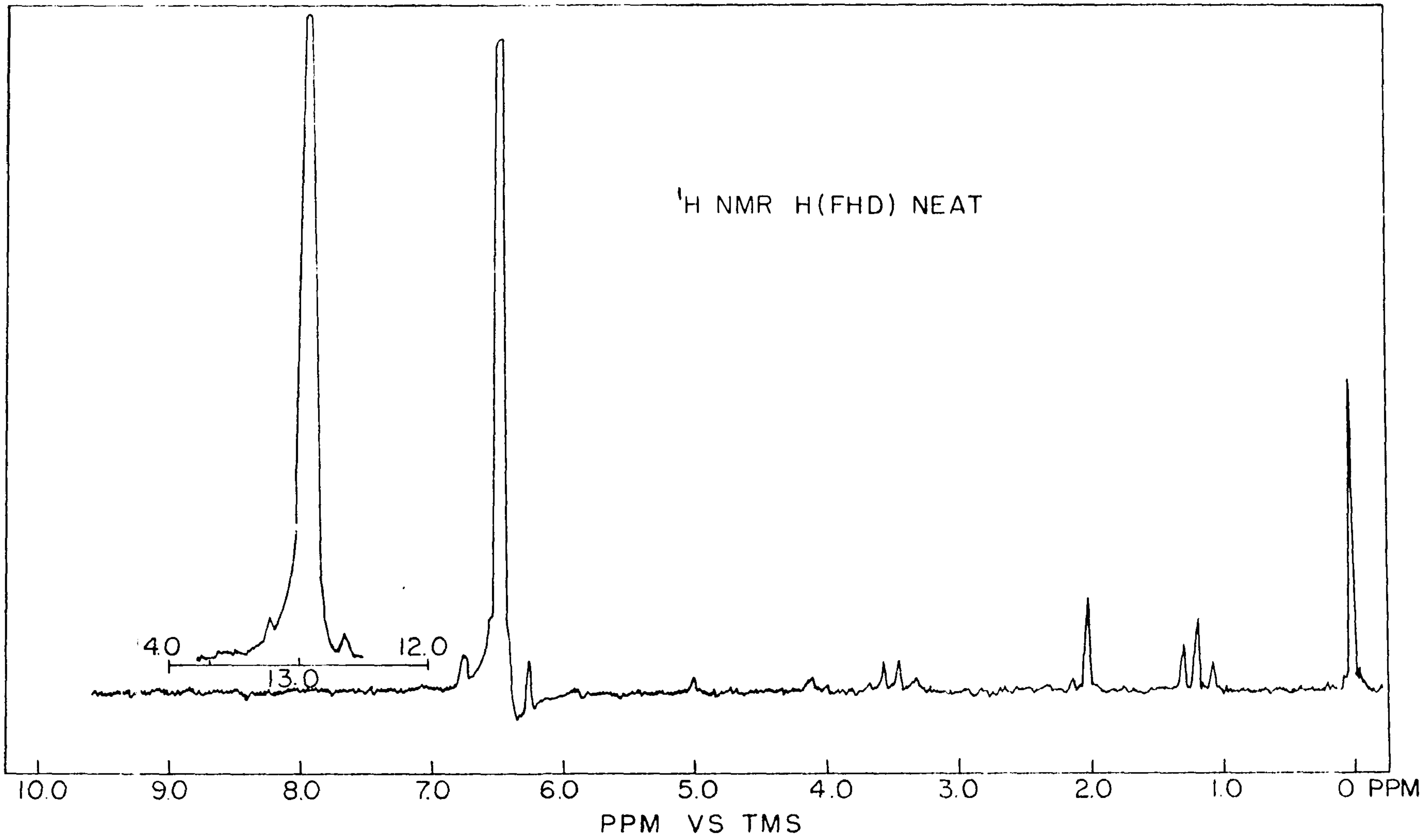


Figure 3.2. ^{1}H nmr spectrum of H(FHD)

1.2 ppm and 3.6 ppm are the result of traces of diethyl ether left after distillation. The keto-enol ratio can be determined by calculating the ratio of integrated band intensities of the 13.0 and 2.0 ppm resonances. By this method the ligand H(FHD) was determined to exist in 98 to 1 enolic form.

The ^{19}F nmr spectrum is shown in Figure 3.3. Chemical shift assignments are given in Table 3.2 and are in good agreement with those reported in the literature for fluorinated β-diketones (111, 164, 167).

Having prepared H(FHD) and proven the structure it was necessary to evaluate the potential of H(FHD) as a reagent for the gas chromatographic determination of the lanthanides. This investigation will be reported in the following two sections.

2. Investigation of lanthanide H(FHD)-TBP mixed-ligand complexes

Sieck (151) has recently demonstrated that the lanthanides could be extracted quantitatively by the synergistic system incorporating H(FHD) and TBP. The theory of synergistic extraction has been discussed in Section I, LITERATURE REVIEW AND THEORY and the experimental details for the synergistic extraction of the lanthanides have been given in the section above, Techniques.

To determine the thermal stability of the mixed-ligand lanthanide complexes, the technique of thermal gravimetric analysis, TGA, was employed.

a. Thermal analysis of H(FHD)-TBP complexes of the lanthanides

Thermal gravimetric analysis is an extremely useful technique in predicting chromatographic success with inorganic chelates. The thermogram indicates whether the compound volatilizes completely

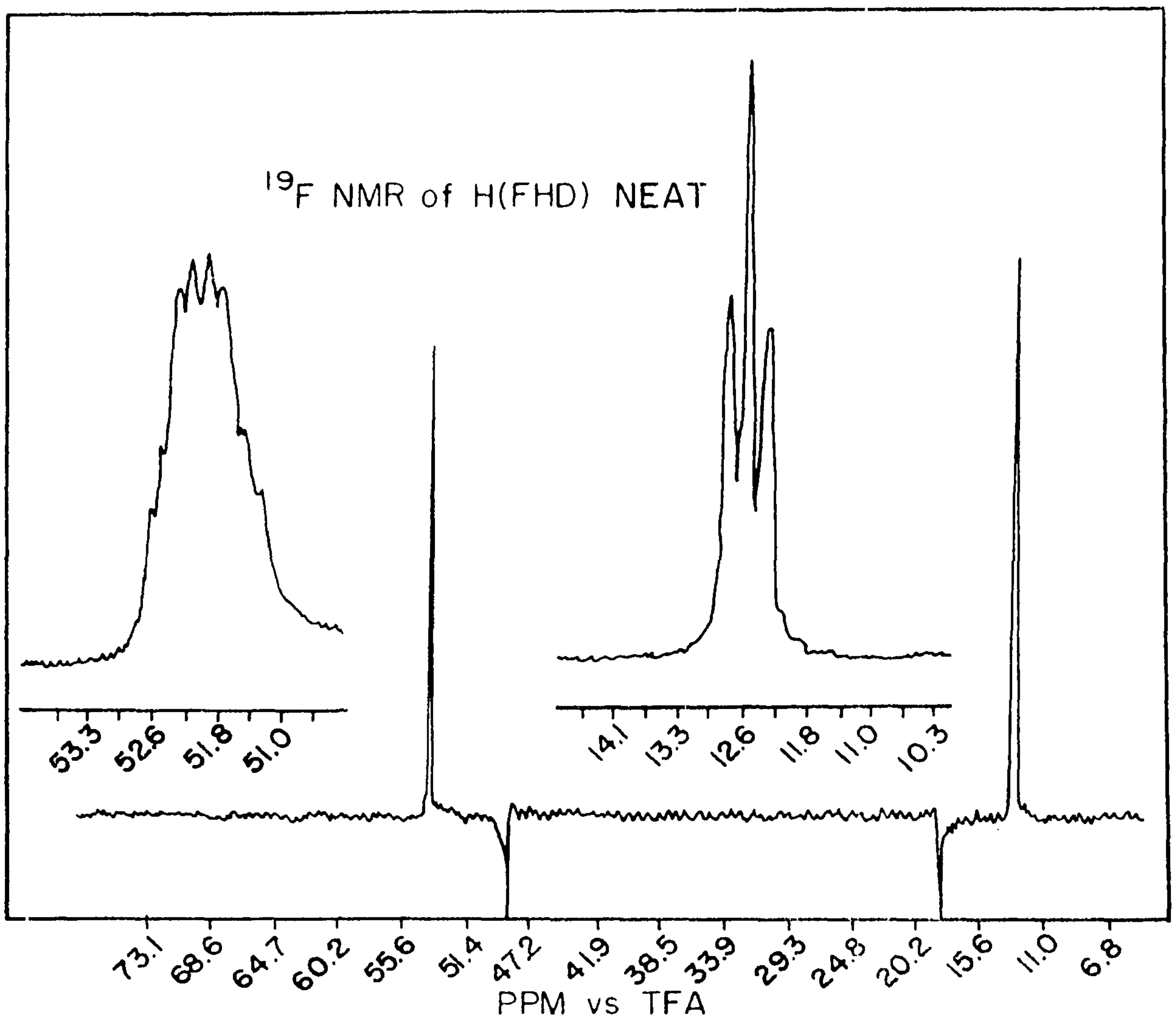
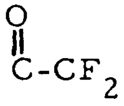
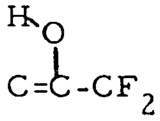


Figure 3.3. ^{19}F nmr spectrum of H(FHD)

Table 3.2 Assignments of ^1H and ^{19}F nmr chemical shifts and infrared spectral bands for H(FHD)

Assignment	^1H nmr (ppm vs TMS)	^{19}F nmr (ppm vs tfa)	IR (cm^{-1})
-OH stretch			3400-2600
-C=C-H			3150
$-CO_2$ (atm)			2380
-C=O			1675
-CF sym. bend			1620
-CF stretch			1320
-CF asym. bend			1205
			1120
-CH (trisub. C=C)			888
CH_2	2.0		
C=C-H	6.5		
enolic H	13.0		
CF_3		9.5	
 $\overset{O}{\overset{\Vert}{C}}-CF_2$		51.8	
 $C=\overset{H\diagdown O}{\overset{\vert}{C}}-CF_2$		51.8	

without decomposition and at reasonable temperatures. It is far better to determine thermal stability by TGA than in the gas chromatographic system. If any decomposition occurs during volatilization only the pan of the TGA unit is fouled. If decomposition occurs in a chromatographic system the column and possibly the detector can be fouled beyond repair. Comparison of the temperature at half-weight for a series of compounds determines any differences in volatility. Quite frequently substantial differences in the volatility allows a gas chromatographic separation by volatility differences alone. The instrumental parameters such as flash volatilization inport temperature and detector temperature may be set after the volatilization temperature of the complex is determined. It is important, however, to remember that the volatilization temperature of the dissolved specie is not necessarily identical to that of the solid complex, because of lattice energy differences.

To obtain pure solid complexes the organic layer of the solvent extraction was withdrawn with a pipet and placed in an evaporating dish. The solvent was then allowed to evaporate. Because of the volatile nature of the complexes, heating of the samples could not be performed. Consequently it was a difficult and time consuming process to remove the excess extraction reagent TBP from the samples. Solid complexes were obtained after air drying for three weeks. Thermal gravimetric data for several of the lanthanide complexes with H(FHD) and TBP are shown in Figure 3.4. Thermal gravimetric data was obtained for all of the lanthanide H(FHD)-TBP complexes, but for clarity only those selected are shown. All of the complexes are thermally stable and volatilize cleanly without residue. Significant differences in

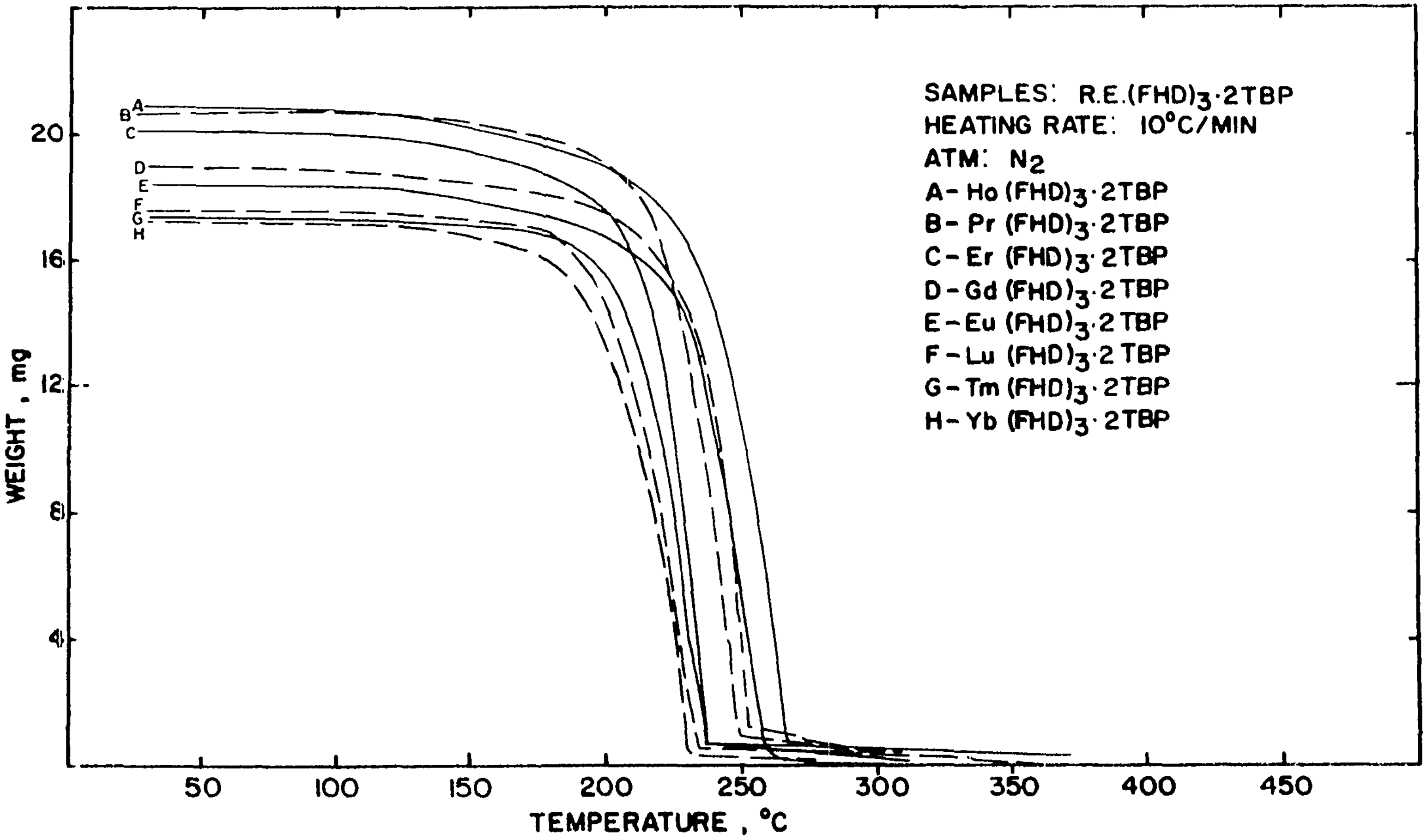


Figure 3.4. Thermograms for H(FHD)-TBP complexes of lanthanides

the temperature of half-weight loss is apparent for many of the complexes. This volatility difference allows the prediction of possible separation based on volatility difference alone. The heavier lanthanides are shown to be volatilized at lower temperature. This observation has been well established by other workers (45, 76, 113, 143, 159) and can be correlated to the size of the ionic radius and the lanthanide contraction. The lanthanides with the smaller ionic radii are the most volatile. This is not restricted to the lanthanides but is manifested in all metal chelate systems. All β-diketonate chelates, regardless of the symmetry of the ligand, have small permanent local dipoles (76). These dipoles would be expected to either decrease in magnitude or become more effectively shielded by a more compact ligand shell as the size of the metal ion is decreased. Furthermore, as the molecular size decreases, the polarizability should be reduced. All of these factors should decrease dipole-dipole, dipole-induced dipole and induced dipole-induced dipole interactions, resulting in increasing volatility as the ionic radius decreases (46, 167). As a result of this constant effect, a useful rule can be derived which allows the prediction of the volatility of metal chelates. For a given ligand system and complexes of identical stoichiometry, the metals with the smallest ionic radii will be the most volatile regardless of the mass of the complex.

The most significant observation from the thermal gravimetric studies is the high thermal stability of the mixed-ligand complexes of lanthanum, cerium, praseodymium and neodymium. In previous studies (13, 25, 122, 146, 148, 151, 167, 171, 172, 173, 180, 181) these metals have been shown to form complexes with β-diketones which are thermally unstable. The formation of thermally stable chelates of these metals represents a major advance in the preparation of complexes suitable for gas chromatographic determination and demonstrates the success of the extraction system in the preparation of chromatographic reagents.

b. Elemental analysis of H(FHD)-TBP complexes of the lanthanides and yttrium Microanalysis was performed on all of the lanthanides and yttrium. Data for these analyses are given in Table 3.3. The complexes are shown to be of the stoichiometry $R.E.(FHD)_3 \cdot 2TBP$, in agreement with that reported for the extracted species as determined by infrared studies (151). During microanalysis it was determined that accurate analysis for carbon and hydrogen could not be obtained because of the formation of volatile compounds by the fluorine liberated with the boron and silicon of the combustion tube. These volatile fluorides were trapped in the Ascarite and Anhydrone and resulted in inconsistent and abnormally poor results. This problem was remedied by the addition of a large ball of silver wire immediately following the combustion tube and the addition of a manganese dioxide trap immediately preceding the Ascarite and Anhydrone traps. This modification was used throughout the studies.

Metal concentration was determined by back extraction with 1.0 N hydrochloric acid and titration of the aqueous layer with EDTA using Xylenol Orange as the indicator. The details of this titration are given in the section on techniques.

A systematic study of the chromatographability of the mixed-ligand complexes was performed. This study was oriented around the performance of columns packed with three different liquid phases.

Table 3.3. Analytical results for mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBP

Compound	% Metal Calcd.	% Metal Found	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found
$Y(FHD)_3 \cdot 2TBP$	5.76	5.80	35.03	35.00	3.72	3.76
$La(FHD)_3 \cdot 2TBP$	8.72	8.80	33.93	33.87	3.61	3.67
$Ce(FHD)_3 \cdot 2TBP$	8.79	8.88	33.91	33.85	3.60	3.61
$Pr(FHD)_3 \cdot 2TBP$	8.79	8.83	33.91	33.91	3.60	3.68
$Nd(FHD)_3 \cdot 2TBP$	9.03	9.18	33.82	33.80	3.59	3.64
$Sm(FHD)_3 \cdot 2TBP$	9.37	9.45	33.69	33.72	3.58	3.63
$Eu(FHD)_3 \cdot 2TBP$	9.46	9.60	33.66	33.71	3.58	3.66
$Gd(FHD)_3 \cdot 2TBP$	9.76	9.84	33.55	33.48	3.57	3.67
$Tb(FHD)_3 \cdot 2TBP$	9.85	9.90	33.51	33.53	3.56	3.61
$Dy(FHD)_3 \cdot 2TBP$	10.05	10.16	33.44	33.40	3.55	3.62
$Ho(FHD)_3 \cdot 2TBP$	10.19	10.28	33.39	33.41	3.55	3.61
$Er(FHD)_3 \cdot 2TBP$	10.32	10.35	33.34	33.30	3.54	3.60
$Tm(FHD)_3 \cdot 2TBP$	10.41	10.51	33.31	33.26	3.54	3.58
$Yb(FHD)_3 \cdot 2TBP$	10.64	10.69	33.22	33.28	3.52	3.56
$Lu(FHD)_3 \cdot 2TBP$	10.74	10.86	33.18	33.09	3.53	3.59

Each liquid phase was studied in detail and will be described in the following section.

c. Evaluation of QF-1 as a liquid phase for the determination of lanthanide H(FHD)-TBP mixed ligand-complexes Although volatile, the mixed-ligand complexes of the lanthanides with TBP required temperatures of up to 220°C for elution. This temperature requirement limits the liquid phases which can be used in columns for the gas chromatography of these complexes. Silicone polymer liquid phases such as SE-30 and QF-1 possess the desired thermal stability.

The liquid phase, QF-1 is a polysiloxane liquid with methyl and 1, 1, 1-trifluoropropyl substituents classified as intermediate in polarity. Columns varying in length from 20 inches to 10 feet x 0.25 inch o.d., were prepared in the liquid phase range of 2 to 25 % w/w QF-1 on Chromosorb W-HP. The H(FHD)-TBP complexes of all of the lanthanides and yttrium were successfully eluted from columns containing QF-1 as the liquid phase at temperatures of 240°C or less.

The extent of partitioning with a gas chromatographic column can be evaluated empirically by measuring the relative retention. When peaks are eluted at retention times longer than that of an unretained solute, partitioning is occurring with the column material. The longer the relative retention time the greater the partitioning. Significant partitioning was observed for the complexes and in general differences in the retention times of individual lanthanides was noted. Although peak shapes were good, a tailing edge was consistently observed. A great deal of preconditioning by concentrated sample injection was required before sample elution was achieved, and spurious peaks were observed frequently. Tailing, sample conditioning and spurious peaks are all indications of non-ideal column interaction or sample decomposition. By trapping eluents from the chromatographic column and comparing infrared spectra with those of samples before elution, it was determined that the samples were being eluted substantially intact. It was therefore concluded that column interaction and not decomposition was the cause of the poor chromatograms. The column interaction could consist of adsorption on the solid support surface; adsorption on the liquid surface; association within the bulk liquid or a combination of these three effects. The precise nature of this interaction will be discussed in Section IV.

Because of this excessive column interaction columns containing QF-1 as a liquid phase were determined to be unsatisfactory for use in the separation and determination of H(FHD)-TBP complexes of the lanthanides.

d. Evaluation of SE-30 as a liquid phase for the determination of lanthanide H(FHD)-TBP mixed-ligand complexes The liquid phase, SE-30, is a non-polar polysiloxane liquid with methyl substituents. Columns varying in length from 20 inches to 10 feet and 0.25 inch o.d., were prepared in the liquid phase range of 2 to 25 % w/w SE-30 on Chromosorb W-HP. It was anticipated that a non-polar phase such as SE-30 would show less column interaction than a polar phase and possibly allow separation of mixtures of the lanthanides by differences in volatility.

All of the lanthanides and yttrium were successfully eluted as mixed-ligand complexes of H(FHD) and TBP. Significant partitioning was found to occur between the complexes and the SE-30. The partitioning was much less than that observed with columns containing QF-1 as the liquid phase. The decrease in partitioning is consistent with the decrease in polarity of the liquid phase. Each chelate produced a sharp symmetrical peak at temperatures less than 240°C. The lighter lanthanides produced peaks which show a slight leading edge. The SE-30 columns did require several sample injections before elution of chelates was achieved. On successive injections the peak observed increased until after six injections a reproducible chromatogram was realized. This "loading" was less severe than that occurring with the columns containing QF-1.

The complexes of highest volatility were eluted first. The differences in retention time roughly correlates with the volatility difference observed during thermal gravimetric analysis. The fact the metals with the smallest ionic radii were eluted earlier is further evidence for the ionic radius effects discussed earlier and allows the addition of a corollary to the previous rule regarding volatilities. In a given chelate system of constant stoichiometry, the metals will be eluted from a gas chromatographic column in order of increasing ionic radii. This corollary allows the correct assignment of peaks from known mixtures with a high degree of confidence even before positive identification by other techniques.

All of the lanthanide H(FHD)-TBP chelates were studied to determine the retention time, relative to cyclohexane, as a function of temperature. Data for this study are shown in Figure 3.5. The instrumental conditions for this experiment were as follows:

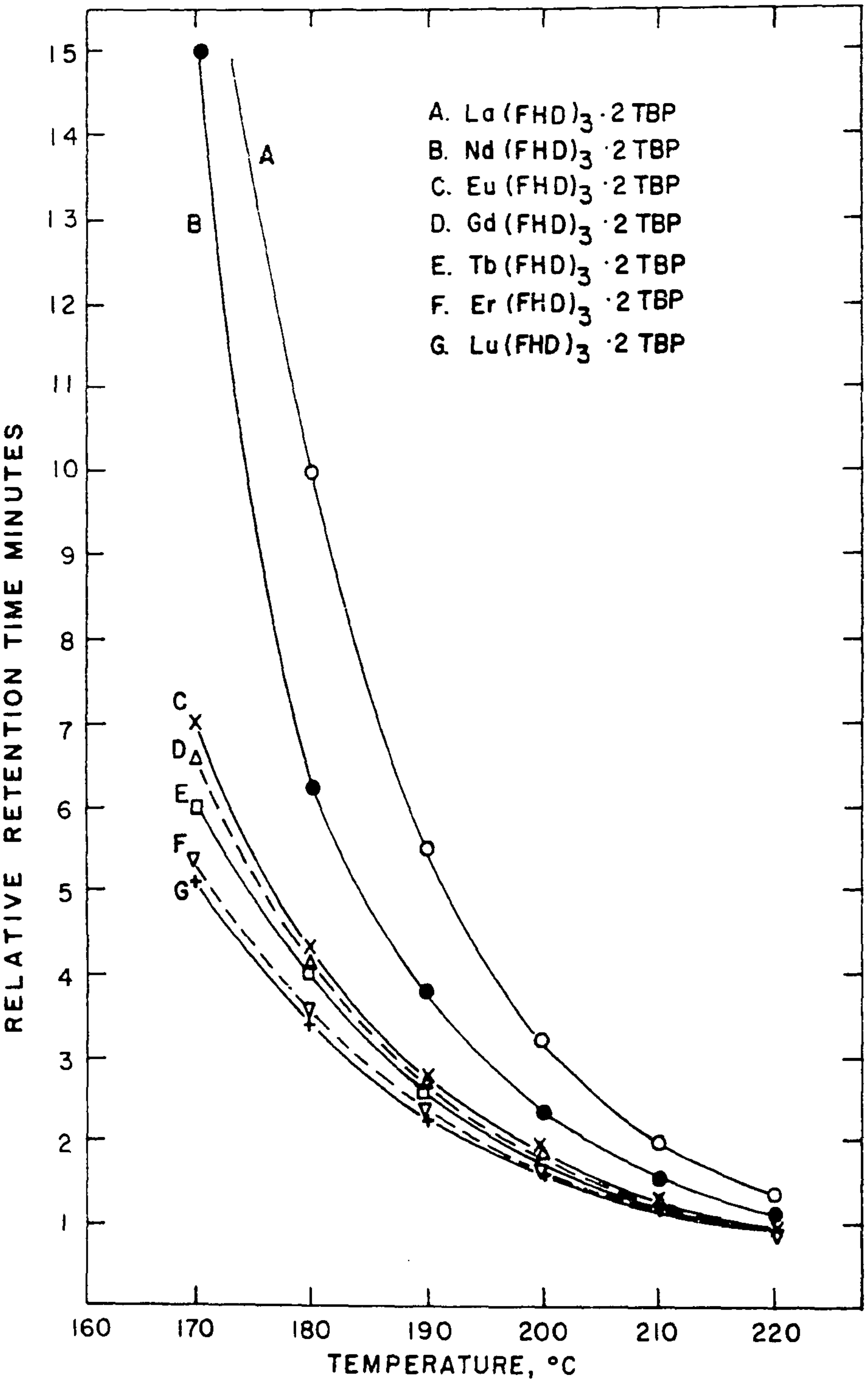


Figure 3.5. Graph of relative retention time as a function of temperature for several lanthanide H(FHD)-TBP complexes

a 4 foot x 0.25 inch o.d. glass column packed with 3.8% SE-30 on Chromosorb W, injection port temperature 300°C, helium carrier flow 50 ml/min, hydrogen 8 psig., air 33 psig., all samples 1.0 μl in volume. As the temperature is lowered the difference in relative retention time increase. This leads to the prediction of better separation at lower temperatures or by a temperature program. The use of lower temperatures is prohibited by the excessive peak broadening and long retention times of the lighter lanthanides. Temperature programming was thoroughly investigated. Using SE-30 columns, mixtures of chelates were eluted in one large peak and no separations were achieved. Even columns ten feet in length did not increase resolution.

The complexes of the lanthanides with H(FHD) and TBP could be eluted from the SE-30 columns, however, the columns were judged unacceptable for the determination of the lanthanides because no separations could be performed and excessive column loading existed.

e. Evaluation of Dexsil 300 GC as a liquid phase for the determination of lanthanide H(FHD)-TBP mixed-ligand complexes

The liquid phase Dexsil 300 GC is a new high temperature, non-polar, liquid phase consisting of carborane cages cross-linked by methyl substituted polysiloxane chains. The structure of Dexsil 300 GC is shown in Figure 3.6. Dexsil 300 GC possesses the most stable thermal range of all liquid phases currently available. As shown by the thermogram in Figure 3.7 Dexsil 300 GC does not volatilize or decompose at temperatures up to 370°C. This high thermal stability makes Dexsil 300 GC extremely useful as a liquid phase for the analysis of metal chelates by gas chromatography.

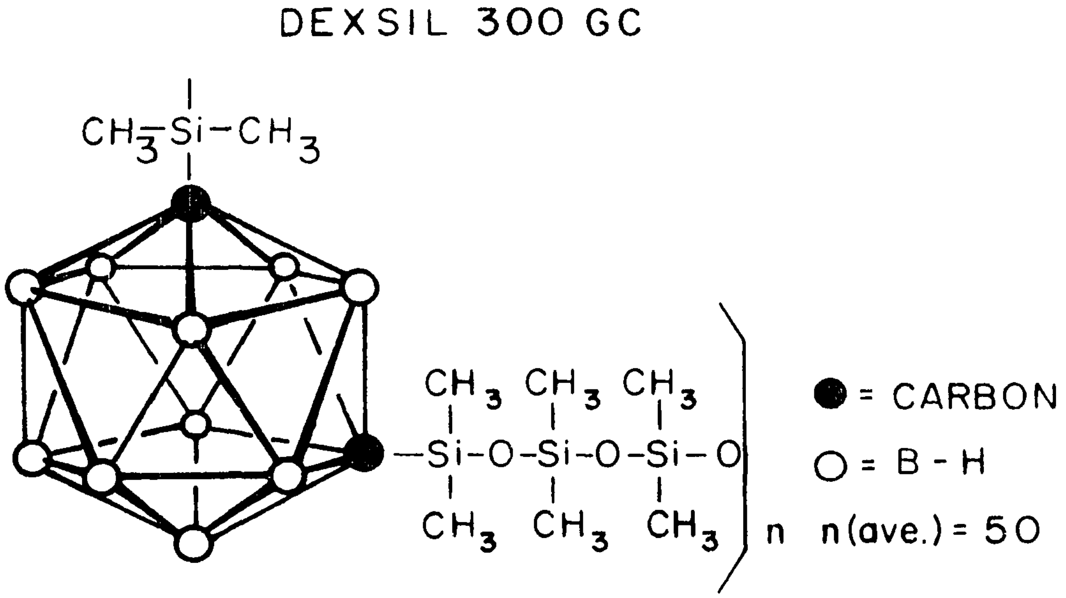


Figure 3.6. Structure of Dexsil 300 GC

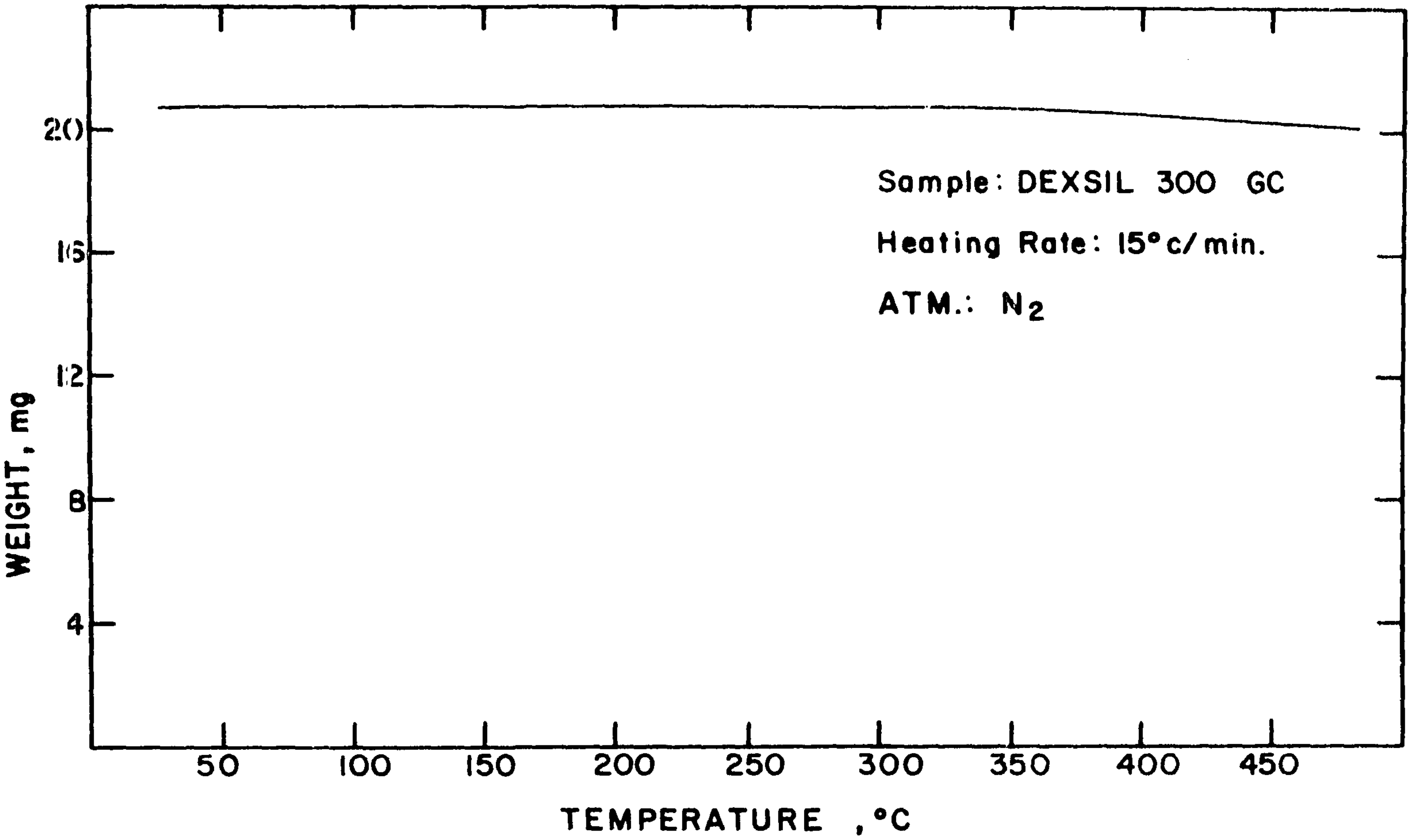


Figure 3.7. Thermogram of Dexsil 300 GC

Columns varying in length from 20 inches to 10 feet x 0.25 inch o.d. were prepared containing liquid phase varying from 2 to 25 % w/w Dexsil 300 GC on Chromosorb W-HP. It was anticipated that the liquid phase would show similar behavior to that of SE-30 because of the similar polar characteristics.

All of the lanthanides and yttrium were successfully eluted as the mixed-ligand complexes of H(FHD) and TBP. The complexes were found to partition significantly with the Dexsil 300 GC. Unlike the columns containing SE-30 and QF-1 liquid phases, no significant conditioning was required before sample elution was achieved. This decrease in column "loading" represents a major improvement in the determination of the lanthanides. Each metal was eluted in a sharp and symmetrical peak as shown in Figure 3.8. All peaks were obtained using a 20 inch x 0.25 inch o.d. stainless steel column containing 6.46 % Dexsil 300 GC on Chromosorb W-HP. A temperature program including a three minute hold at 172°C and then a 6°C/minute linear increase was used. The other conditions were: FID 290°C, nitrogen carrier flow 50 ml/min., air 33 psig., and hydrogen 8 psig. The heavier lanthanides were eluted at relative retention times which were very near the relative retention time of the excess TBP present in the extraction mixture. This similarity in retention time resulted in some peak over lap.

Various column lengths were studied. Columns of 4 feet x 0.25 inch o.d. or less in length performed with higher efficiency than the longer columns which showed a high degree of band spreading.

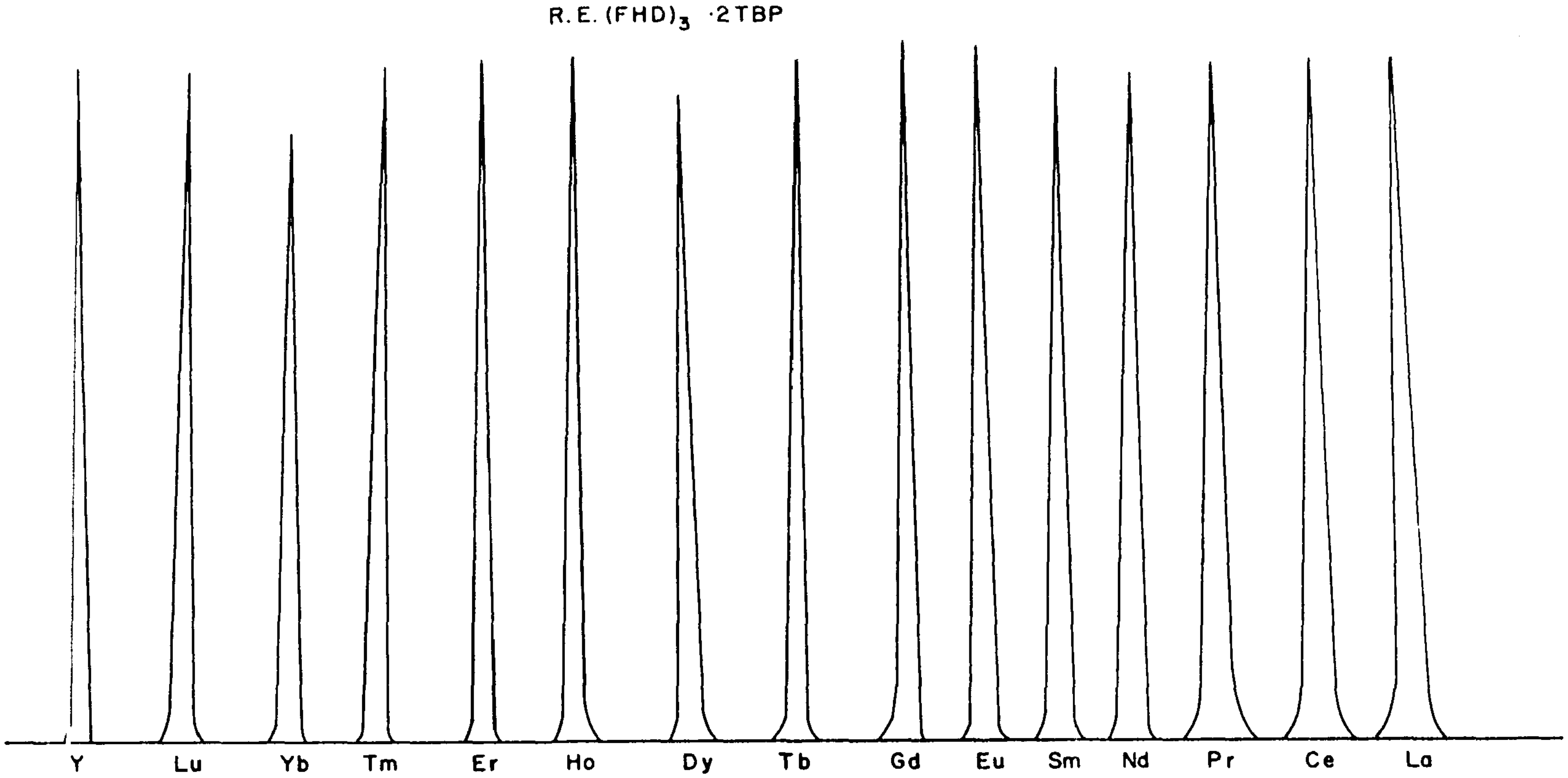


Figure 3.8. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and TBP

Throughout the study it was found that longer columns performed less efficiently. Characteristically the metal chelates have wide peak widths. As the length of the column increased the peak widths increased. This increase in peak width negates any improvement in separations. Furthermore, the retention time becomes excessively long with higher temperatures required for elution as column length increases. The sharpest peaks, eluted at the lowest temperature and in the least time, were obtained using 20 inch x 0.25 inch columns.

No evidence of metal exchange, reaction and/or decomposition of the metal chelates on the hot metal surface of the stainless steel columns was observed. The chelates produced identical chromatograms when eluted from columns prepared from either glass or stainless steel.

The unusually high quality of the chromatographic peaks obtained when using the columns packed with support containing Dexsil 300 GC promoted further studies into the partitioning of the chelates.

Veening and Huber(183) have reported studies on retention of metal chelates. They have shown the partition ratio, $\underline{k}$, to be a function of the phase ratio, $\underline{q}$, for different chelates, as shown in the following equation:

$$k = Kq \tag{3.7}$$

where K is the partition coefficient and $\underline{q}$ is the phase ratio or ratio of the volume of the liquid phase to the volume of the column. The relationship of the partition coefficient to retention behavior was discussed in Section II. Experimentally the partition ratio can be easily obtained according to the following equation:

$$k = (t_r - t_{r_o})/t_{r_o} \tag{3.8}$$

where t_r is the retention time of the solute in minutes and t_{r_o} is the retention time of an unretained solute, such as air or methane, in minutes. The phase ratio is related to the weight of the liquid phase by a constant, (density of liquid phase x gas volume)$^{-1}$.

For this study methane was used to determine the value of t_{r_o} and the partition ratio was calculated for each of the lanthanides using Equation 3.8. As the amount of liquid increased, the relative retention time and, therefore, the partition ratio increased. The performance of the column decreased markedly with high percentages of Dexsil 300 GC. The retention time became excessively long and the peaks became excessively wide. Columns of ten feet in length packed with 20 % Dexsil 300 GC were found to have such high partition ratios that no usable elution patterns could be obtained. The variation of partition ratio, $\underline{k}$, with the trivalent ionic radii of the lanthanides is shown in Figure 3.9. It is clear from this plot that significant differences in $\underline{k}$ values are realized for the lanthanides. The order of partition ratios, increasing as ionic radius increases, is yet further evidence of the volatility-ionic radius relationship. Even yttrium with mass approximately half that of erbium has a partition ratio in agreement with that predicted by its ionic radius.

Peak shape improved by using a temperature program. The temperature program has the effect of increasing differences in partition ratios for the heavier lanthanides while maintaining constant partition ratio differences for the lighter lanthanides. The time for elution and the sharpness of the peaks, is also improved by the use

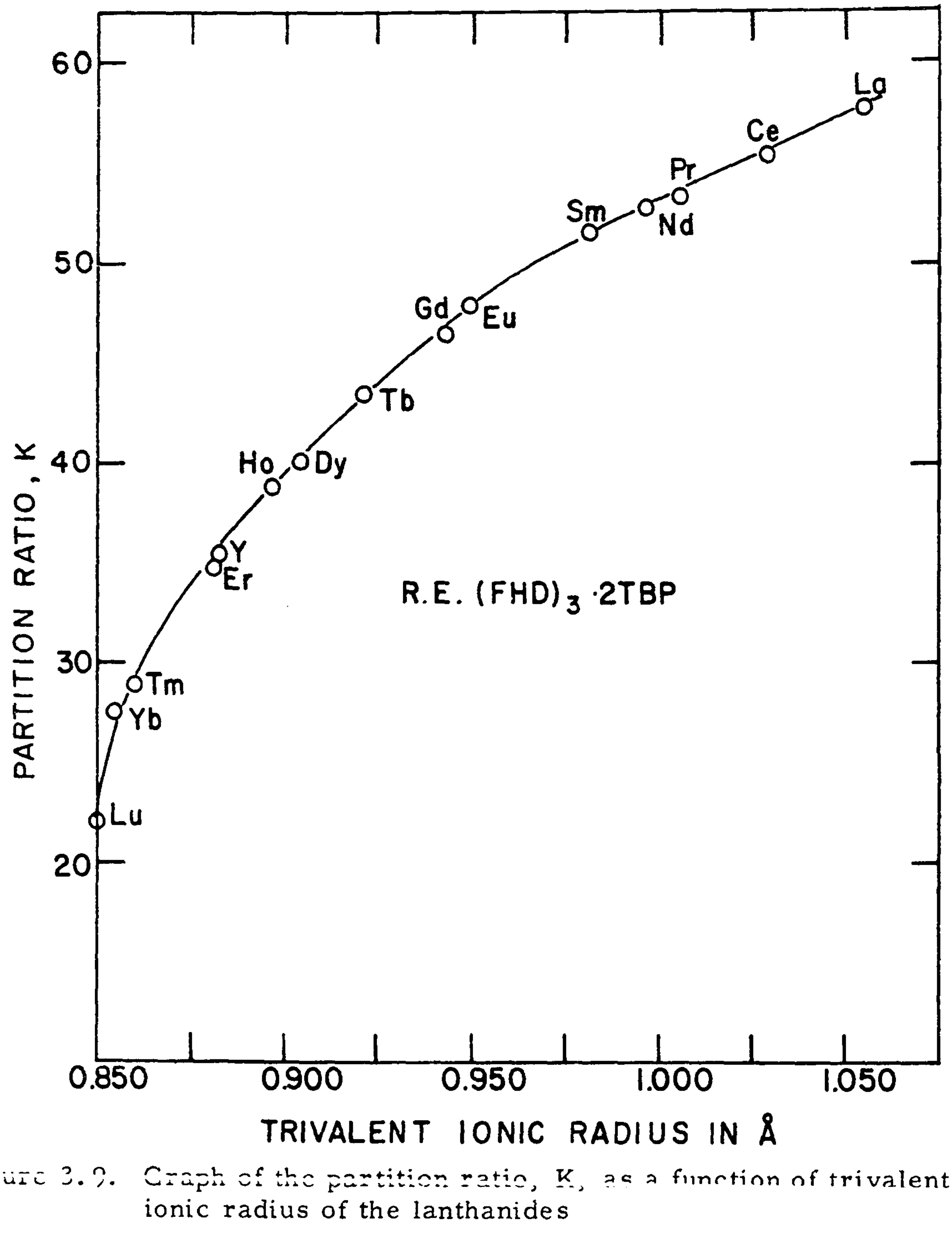


Figure 3.9. Graph of the partition ratio, K, as a function of trivalent ionic radius of the lanthanides

of a temperature program.

Using the appropriate temperature program, several successful separations were achieved. Figure 3.10 shows the separation of praseodymium and europium; and gadolinium and terbium. The separation of gadolinium and terbium illustrates the separation of two adjacent lanthanides. Figure 3.11 and Figure 3.12 illustrate the separation of a mixture of erbium, terbium and neodymium and a mixture of ytterbium, holmium, terbium, europium and praseodymium. For the most part, these separations are good and are suitable for quantitative analysis with electronic integration.

Quantitative data for several of the individual lanthanides are given in Table 3.4. Analytical data for a few mixtures of the lanthanides are summarized in Table 3.5. Calibration curves of peak area vs concentration of metal were prepared using standard solutions. The standard solutions were prepared by the identical solvent extraction procedure as the unknowns. The analytical curves were linear in the concentration range 10^{-5} to 10^{-7} g metal. At lower concentrations the peaks became cigar shaped in appearance indicating column over load. All analytical curves have non-zero intercepts, with zero response for samples of finite concentration. The non-zero intercept is either a result of the still present, though significantly lower, column "loading", or a measure of the lower detection limit of the FID detector. Several injections of the lanthanides at low concentration levels were made and the chromatographic eluents collected in glass collection traps. Subsequent fluorescence analysis of the trappings failed to give evidence of chelate elution. By heating the column to 320°C some of the complex

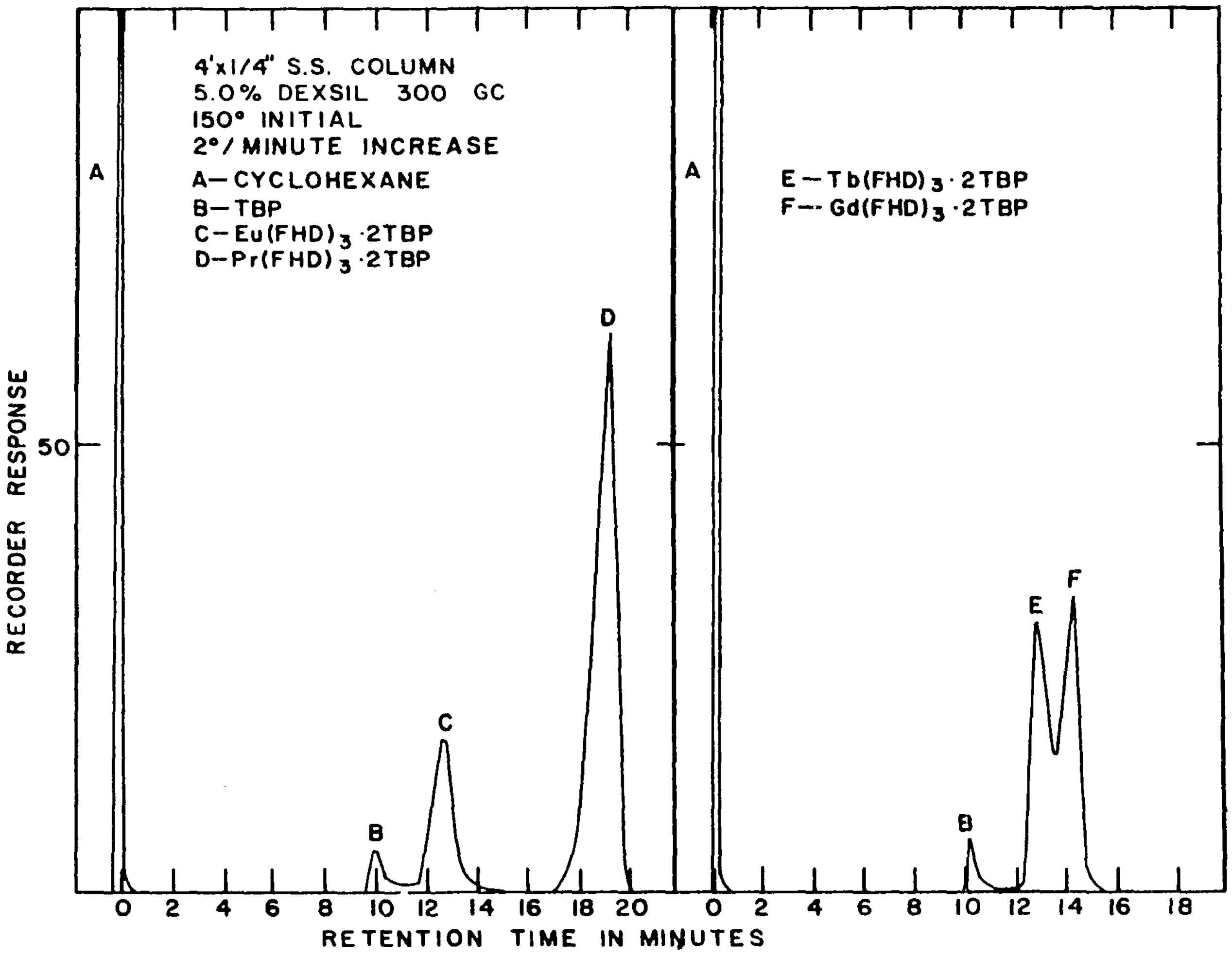


Figure 3.10. Gas chromatograms of mixtures of several lanthanide H(FHD)-TBP complexes

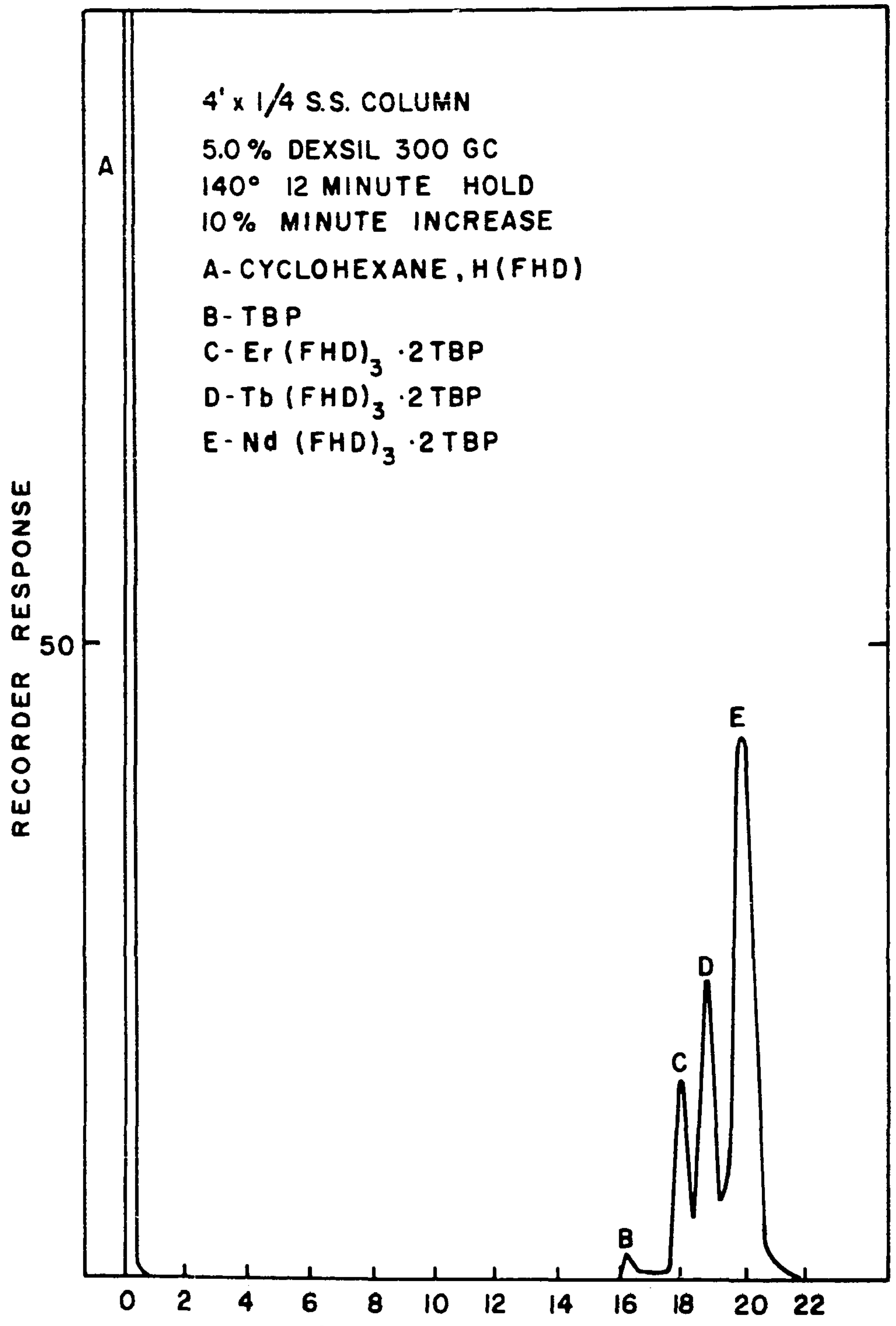


Figure 3.11. Gas chromatogram of a mixture of $Er(FHD)_3 \cdot 2TBP$, $Tb(FHD)_3 \cdot 2TBP$ and $Nd(FHD)_3 \cdot 2TBP$

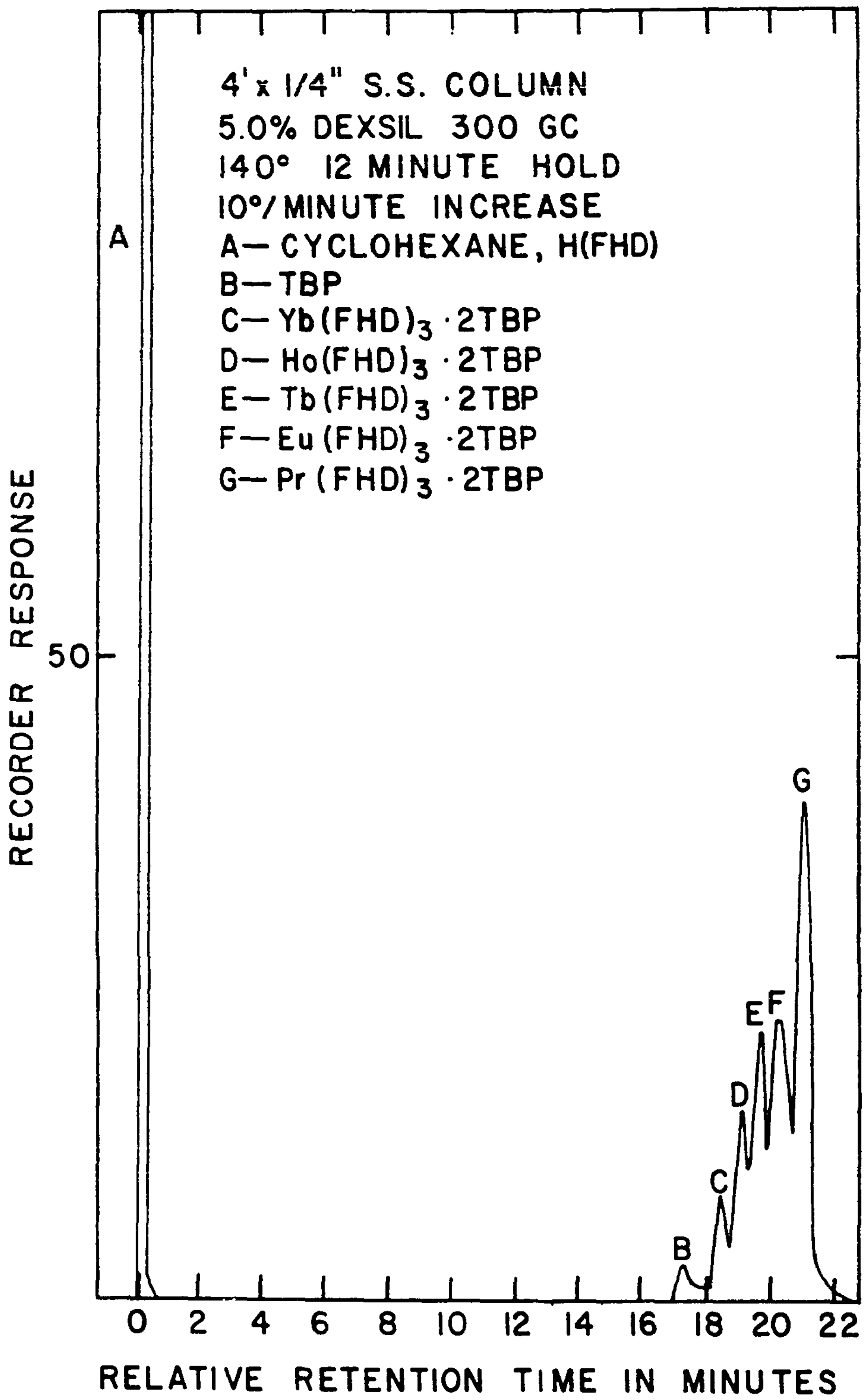


Figure 3.12. Gas chromatogram of a mixture of $Yb(FHD)_3 \cdot 2TBP$, $Ho(FHD)_3 \cdot 2TBP$, $Tb(FHD)_3 \cdot 2TBP$, $Eu(FHD)_3 \cdot 2TBP$ and $Pr(FHD)_3 \cdot 2TBP$

Table 3.4. Analysis of selected lanthanide H(FHD)-TBP mixed-ligand complexes

Compound	Actual Conc. in μgrams	Conc. Found in μgrams	Relative error in %
$Pr(FHD)_3 \cdot 2TBP$	0.91	1.01	+10.98
$Eu(FHD)_3 \cdot 2TBP$	1.16	1.07	-7.76
$Er(FHD)_3 \cdot 2TBP$	2.19	2.11	-3.65
$Yb(FHD)_3 \cdot 2TBP$	1.69	1.78	+5.33

Table 3.5. Analysis of mixtures of lanthanide H(FHD)-TBP mixed-ligand complexes

Compound	Actual Conc. in μgrams	Conc. Found in μgrams	Relative error in%
$Yb(FHD)_3 \cdot 2TBP$	1.02	1.08	+6.67
$Eu(FHD)_3 \cdot 2TBP$	0.87	0.84	-3.33
$Er(FHD)_3 \cdot 2TBP$	0.86	0.77	-10.46
$Pr(FHD)_3 \cdot 2TBP$	0.64	0.76	+18.75

was purged from the column. Since the chelate is apparently not eluted at low levels and can be purged from the column, it is probable that the non-zero intercept results from column "loading".

To correct for peak overlap observed in the analysis of mixtures, analytical curves were prepared from standard solutions containing the elements of interest in an equal concentration ratio. These analytical curves were found to be usable for a period of two weeks.

In general, the analytical data are within ± 10 % of the actual value. The random nature of the error is probably caused by the inaccuracy of sample size measurement and errors in area measurement by disc integration.

During the course of this study it was noted that several of the chelates exhibited different flame ionization detector responses. In particular, samarium and europium gave a high degree of flame enhancement. By measuring the integrated area of each peak for several sample concentrations the response factor of the FID can be calculated. The response factor is defined as the detector response in integration counts per μgram of sample component. Response factors for the H(FHD)-TBP mixed-ligand complexes of the lanthanides are given in Table 3.6. The differences in flame response are probably a result of different combustion properties of the individual lanthanides in the flame.

Considerable success was realized with the mixed-ligand lanthanide complexes of H(FHD) and TBP and the Dexsil 300 GC columns. This system is suitable for the quantitative determination of the lanthanides in selected mixtures and individually. As a result of the failure in

Table 3.6. Response factors for flame ioniztion detector

Compound	Response factor in integration cnts. x 10^{-5}/μg
$Lu(FHD)_3 \cdot 2TBP$	10.80
$Yb(FHD)_3 \cdot 2TBP$	5.10
$Tm(FHD)_3 \cdot 2TBP$	13.20
$Er(FHD)_3 \cdot 2TBP$	39.12
$Ho(FHD)_3 \cdot 2TBP$	15.42
$Dy(FHD)_3 \cdot 2TBP$	27.06
$Tb(FHD)_3 \cdot 2TBP$	12.06
$Gd(FHD)_3 \cdot 2TBP$	16.32
$Eu(FHD)_3 \cdot 2TBP$	41.74
$Sm(FHD)_3 \cdot 2TBP$	136.20
$Nd(FHD)_3 \cdot 2TBP$	12.90
$Pr(FHD)_3 \cdot 2TBP$	6.66
$Ce(FHD)_3 \cdot 2TBP$	18.90
$La(FHD)_3 \cdot 2TBP$	1.65

attaining resolution of lutetium from the excess TBP and the limited number of separations that could be performed, an investigation into the mixed-ligand complexes of DBSO was performed. The results of this investigation are reported in the following sections..

3. Investigation of lanthanide H(FHD)-DBSO mixed-ligand complexes

Sieck (151) has recently demonstrated the quantitative synergistic extraction of the lanthanides by H(FHD) amd DBSO. The theory of synergistic extraction has been discussed in Section I, LITERATURE REVIEW AND THEORY, and the experimental details for the synergistic extraction of the lanthanides have been described above in the section on Techniques. Before the complexes were studied by gas chromatography their thermal stability was determined by thermal gravimetric analysis.

a. Thermal analysis of H(FHD)-DBSO mixed-ligand complexes of the lanthanides The mixed-ligand complexes of the lanthanides with DBSO were prepared by the solvent extraction procedure described in the section on techniques. The two phases were then separated by pipet and the organic layer placed in an evaporating dish. The solvent and excess solvent extraction reagents were then allowed to evaporate. The DBSO complexes remained in a semi-crystaline oil even after three weeks drying time. The resultant oils were studied by the technique of thermal gravimetric analysis. Thermal gravimetric data was obtained for all of the lanthanide mixed-ligand complexes with H(FHD) and DBSO. Thermograms for several of the lanthanides are shown in Figure 3.13. For clarity only those selected are shown. All of the complexes are thermally stable volatilizing cleanly without

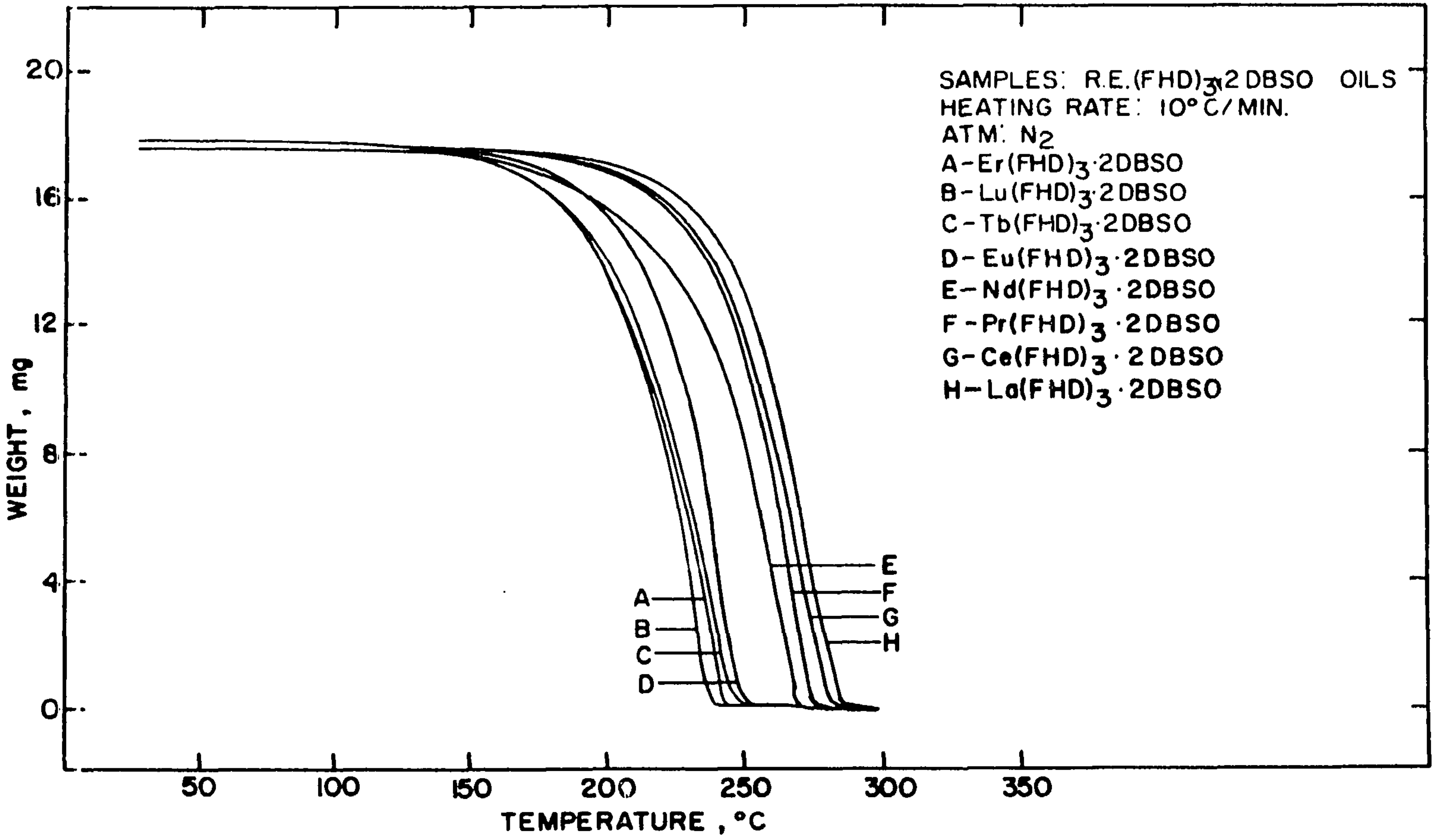


Figure 3.13. Thermograms for H(FHD)-DBSO complexes of the lanthanides

residue. Significant differences in the temperature at half-weight are apparent for many of the complexes, however, volatility differences for the heavy lanthanides are only slight. This evidence indicates that if separations are to be effected with the heavy lanthanides, they must be based on differences in partitioning, not only on volatility difference. The empirical rule predicting volatilities of metal complexes is shown once again to be valid. The most volatile complexes are those with the smallest ionic radii.

The most significant observation from the thermal gravimetric studies is the high thermal stability of the mixed-ligand complexes of lanthanum, cerium, praseodymium and neodymium. In previous studies (13, 25, 122, 146, 148, 151, 167, 171, 172, 173, 180, 181) these metals have been found to form thermally unstable complexes. The formation of thermally stable chelates of these metals represents a major advance in the preparation of complexes suitable for gas chromatographic determination and further demonstrates the success of the extraction system in the preparation of chromatographic reagents.

b. Elemental analysis of H(FHD)-DBSO complexes of the lanthanides and yttrium Microanalysis was performed on all of the H(FHD)-DBSO complexes of the lanthanides and yttrium. Data for the analyses are given in Table 3.7. The complexes are of the stoichiometry R. E. $(FHD)_3 \cdot 2DBSO$, in agreement with that reported for the extracted species as determined by infrared studies (151). The modifications in the combustion apparatus described above, were used when performing all microanalyses.

The metal concentration was determined by back extraction with

Table 3. 7. Analytical results for mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and DBSO

	% Metal		% Carbon		% Hydrogen	
Compound	Calcd.	Found	Calcd.	Found	Calcd.	Found
Y(FHD)$_3$·2DBSO	6.66	6.82	33.31	33.23	2.95	2.98
La(FHD)$_3$·2DBSO	10.01	10.12	32.03	32.09	2.83	2.80
Ce(FHD)$_3$·2DBSO	10.09	10.18	32.00	31.98	2.83	2.84
Pr(FHD)$_3$·2DBSO	10.09	10.11	32.00	31.90	2.83	2.86
Nd(FHD)$_3$·2DBSO	10.35	10.43	31.91	31.85	2.82	2.84
Sm(FHD)$_3$·2DBSO	10.75	10.81	31.76	31.71	2.81	2.85
Eu(FHD)$_3$·2DBSO	10.85	10.82	31.73	31.68	2.81	2.86
Gd(FHD)$_3$·2DBSO	11.21	11.25	31.68	31.65	2.80	2.84
Tb(FHD)$_3$·2DBSO	11.32	11.33	31.64	31.60	2.80	2.86
Dy(FHD)$_3$·2DBSO	11.54	11.61	31.56	31.53	2.79	2.84
Ho(FHD)$_3$·2DBSO	11.69	11.77	31.51	31.49	2.79	2.83
Er(FHD)$_3$·2DBSO	11.84	11.96	31.46	31.44	2.78	2.77
Tm(FHD)$_3$·2DBSO	11.94	12.04	31.42	31.38	2.78	2.80
Yb(FHD)$_3$·2DBSO	12.20	12.25	31.33	31.29	2.77	2.80
Lu(FHD)$_3$·2DBSO	12.32	12.28	31.26	31.28	2.95	2.98

1.0 N hydrochloric acid and titration of the aqueous layer with EDTA using Xylenol Orange as the indicator (81).

The complexes of H(FHD) and DBSO were volatile, thermally stable and of known composition. A systematic study of the chromatographic performance on columns containing SE-30, QF-1 and Dexsil 300 GC as liquid phases, was performed so that the utility of the mixed-ligand system as a gas chromatographic system could be determined. This study is described in detail in the following sections.

c. Evaluation of QF-1 as a liquid phase for the determination of lanthanide H(FHD)-DBSO mixed-ligand complexes Columns varying in length from 20 inches to 10 feet and 0.25 inch o.d., were prepared in the liquid phase range of 2 to 25 % w/w QF-1 on Chromosorb W-HP. All of the lanthanides and yttrium were successfully chromatographed at temperatures of less than 240°C. A significant partitioning by the chelates with the liquid phase was indicated by the relative retention times observed. This partitioning was substantially greater than that observed with TBP containing complexes, and is probably a result of the increased polar nature of the chelates caused by the addition of the polar DBSO molecule as neutral donor. The increase in partitioning made long columns unsuitable for analysis because of excessively large peak widths and lengthy retention times. With short columns the peak shapes were generally sharp but all possessed a long tailing edge. Frequent observations of chelate displacement and excessive column loading characterized the columns containing QF-1.

The presence of this excessive column interaction precluded the use of QF-1 as a liquid phase for the determination of H(FHD)-DBSO mixed-ligand complexes.

d. Evaluation of SE-30 as a liquid phase for the determination of lanthanide H(FHD)-DBSO mixed-ligand complexes Columns varying in length from 20 inches to 10 feet and 0.25 inch o.d., were prepared in the liquid phase range of 2 to 25 % w/w SE-30 on Chromosorb W-HP. All of the lanthanides and yttrium were successfully eluted as the mixed-ligand complexes of H(FHD) and DBSO. The partitioning was greater than that observed with theTBP containing chelates, but was much less than that observed with the QF-1 columns. Each chelate produced a sharp symmetrical peak at temperatures of 240° C or less. The lighter lanthanides produced peaks showing a leading edge. Several sample injections were required before reproducible elution was observed for the chelates. This "loading" was less than that observed with the columns containing QF-1.

Several attempts were made at the separation of lanthanides as the H(FHD)-DBSO chelates but no success was realized, even under the conditions of temperature programming. Various column lengths were tried, but the increase in peak width, as column length increased, precluded any increase in column efficiency.

In the absence of successful separations and the existence of extensive column phenomena, SE-30 was considered unsatisfactory for use as a liquid phase for the gas chromatographic determination of the lanthanides as H(FHD)-DBSO chelates.

e. Evaluation of Dexsil 300 GC as a liquid phase for the determination of lanthanide H(FHD)-DBSO mixed-ligand complexes Columns varying in length from 20 inches to 10 feet and 0.25 inch o.d., were prepared containing liquid phase varying from 2 to 25 % w/w Dexsil 300 GC on Chromosorb W-HP. All of the lanthanides and yttrium were successfully eluted as the mixed-ligand complexes of H(FHD)-DBSO. The complexes were found to partition to a greater extent than those complexes containing TBP. Unlike the liquid phases SE-30 and QF-1, no appreciable prior sample conditioning was required before reproducible sample elutions were achieved. Each metal was eluted in sharp symmetrical peaks as shown in Figure 3.14. All peaks were obtained using a 20 inch x 0.25 inch, stainless steel column, temperature programed with 172°C hold for three minutes, then increased at 6°C/minute; FID 290°C, inport 290 °C and nitrogen carrier flow of 50 ml/minute. Significantly, the heavier lanthanides were all resolved from the peak produced by the excess DBSO present in the extraction system. The separation of the chelates from the excess extraction reagents represents a major improvement in the determination of the lanthanides and allowed quantitative work even with the heavy lanthanides.

Both glass and stainless steel columns were studied. No evidence of metal exchange, reaction and/or decomposition of the metal chelates on the hot metal surface of the stainless steel was observed. Columns of greater than four feet in length were found to be unsatisfactory because of increased peak width. The optimum column length was 20 inches x 0.25 inch o.d.. Short columns allowed rapid elution from columns of high liquid phase percentages, at lower temperatures.

To determine the optimum percentage of liquid phase for

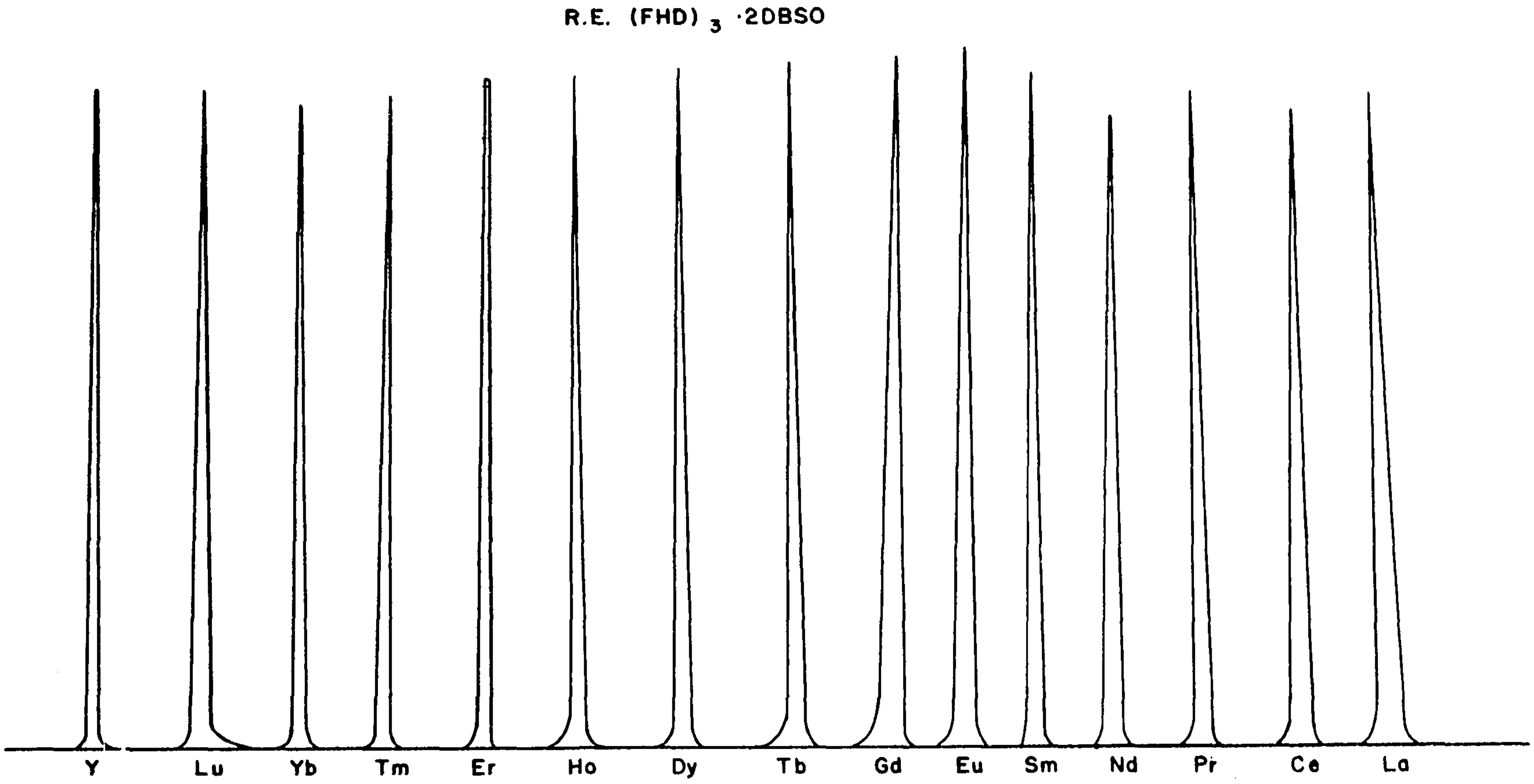


Figure 3.14. Gas chromatographic peaks for the mixed-ligand complexes of the lanthanides and yttrium with H(FHD) and DBSO

separation, the relationship between relative retention time and the amount of Dexsil 300 GC present was investigated. Figure 3.15 presents the relative retention time as a function of percent Dexsil 300 GC. It is evident from this plot that optimum separation of the yttrium group lanthanides, gadolinium through lutetium, could be achieved using a column containing approximately 10 % Dexsil 300 GC. The optimum separation of the cerium group lanthanides, lanthanum through europium, could be achieved with columns containing approximately 5 % Dexsil 300 GC. It is apparent that a temperature program could enhance separations by allowing the maximum difference in relative retention time at all times while still eluting the chelates in sharp peaks. This effect is illustrated by Figure 3.16 in which the partition ratio, $\underline{k}$, as calculated by Equation 3.8, is plotted as a function of the trivalent ionic radius. A 20 inch x 0.25 inch stainless steel column packed with 6.46 % Dexsil 300 GC was used for this study. The temperature was held at 172°C for three minutes then linearly increased at 6°C/minute. Significant differences in the partition ratio for all of the lanthanides can be seen. Again the effect of ionic radius is manifested, with the heavier lanthanides being eluted at lower temperature.

Using this column many excellent separations were performed as shown in Figure 3.17. Figure 3.18 shows the first reported successful separation of adjacent lanthanides. Although the resolution is not complete, electronic integration could be utilized to obtain quantitative data. Figure 3.19 illustrates the quantitative resolution of a mixture of the lanthanides metals on an every-other-one basis.

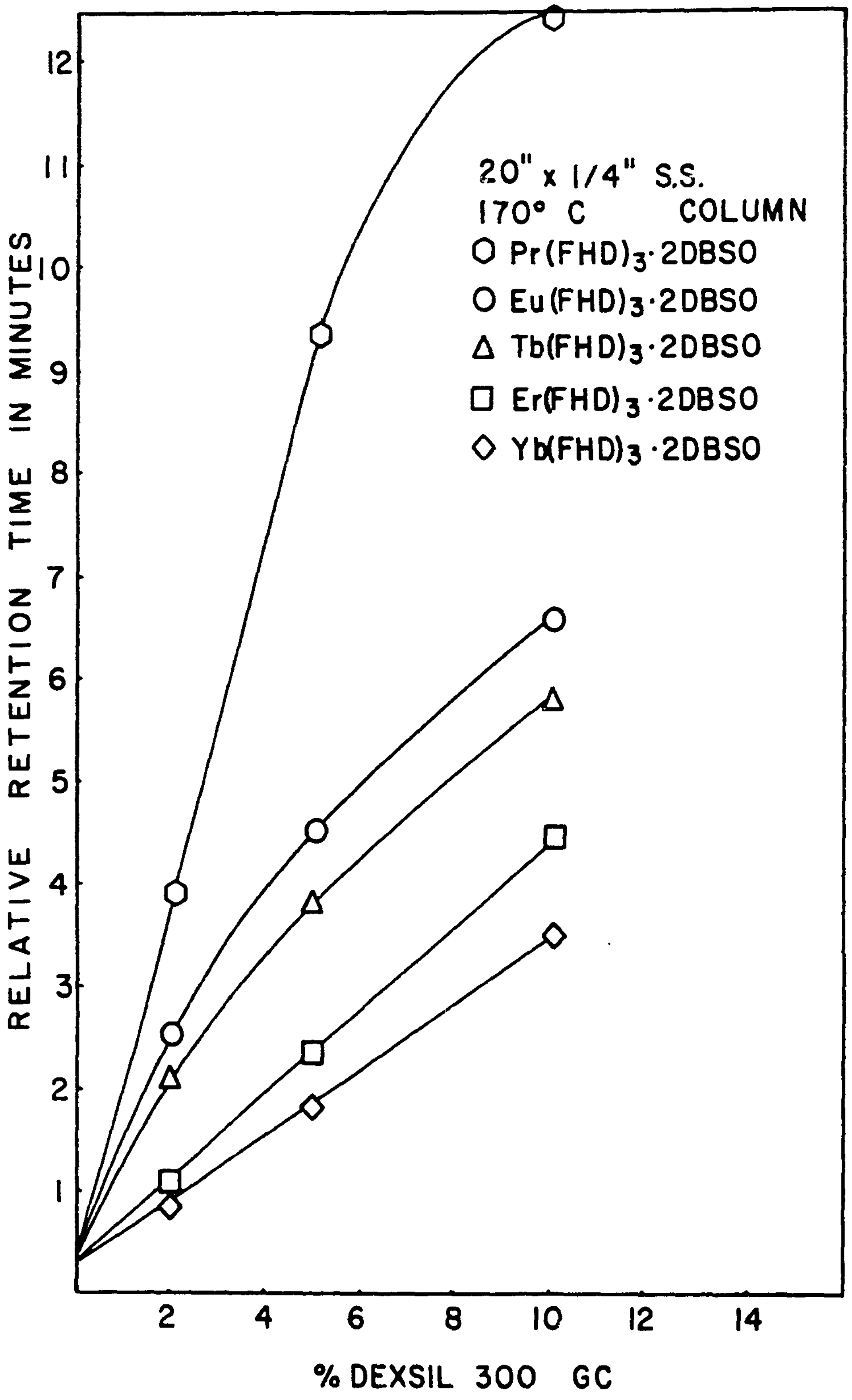


Figure 3.15. Graph of the relative retention of several lanthanide H(FHD)-DBSO complexes as a function of the % Dexsil 300 GC

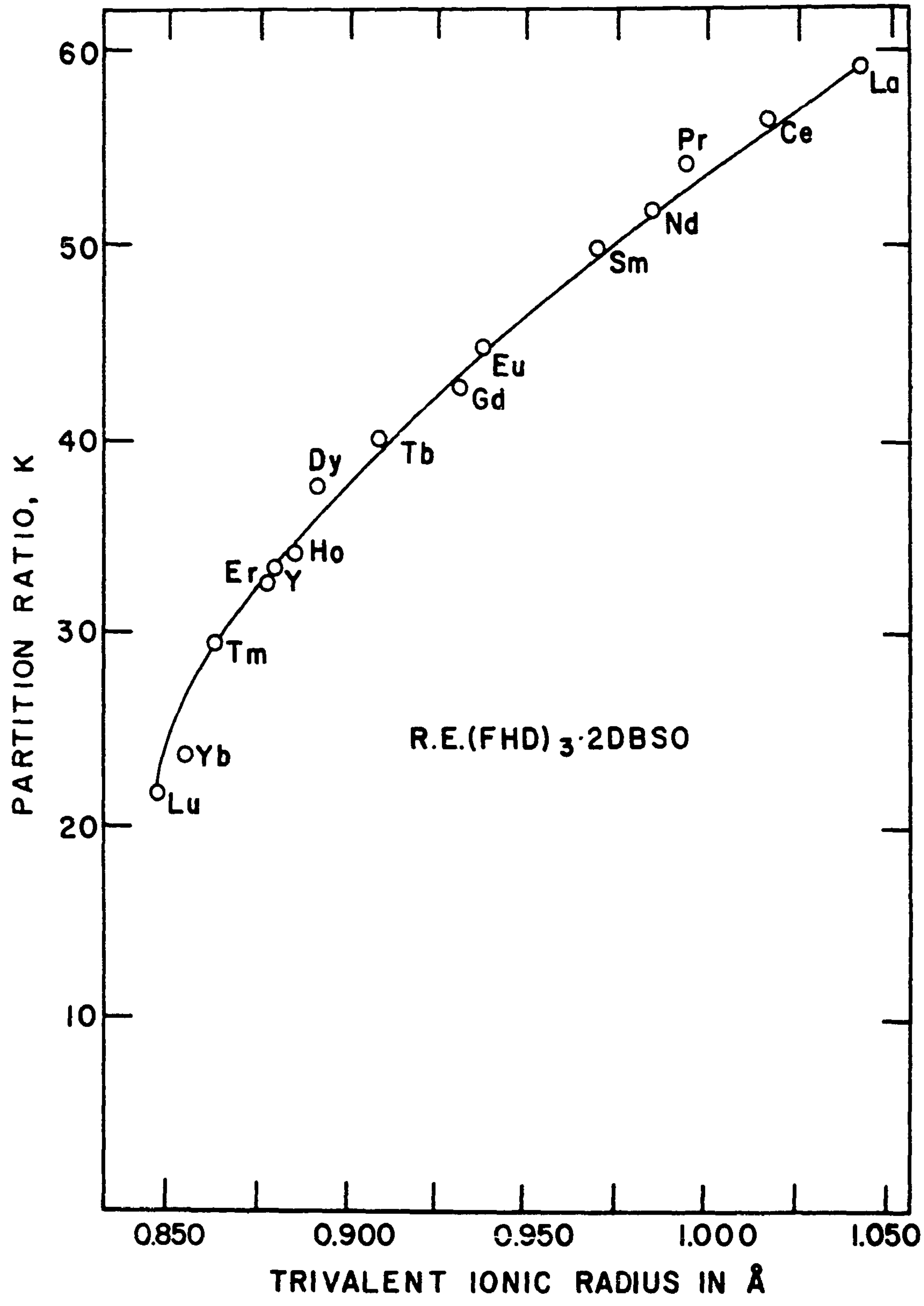


Figure 3.16. Graph of the partition ratio, k, as a function of the trivalent ionic radius of the lanthanides

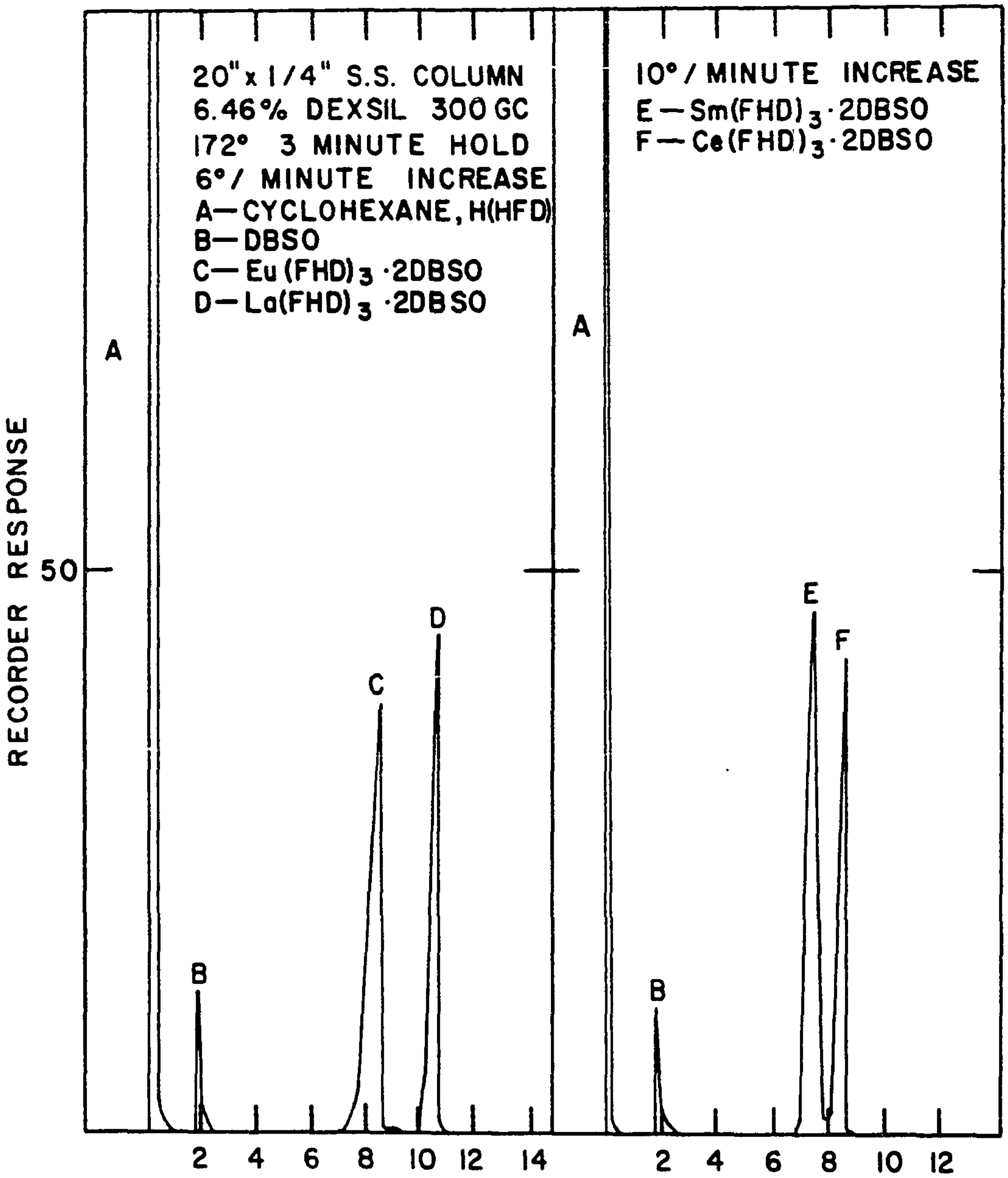


Figure 3.17. Gas chromatograms of mixtures of several lanthanide H(FHD)-DBSO complexes

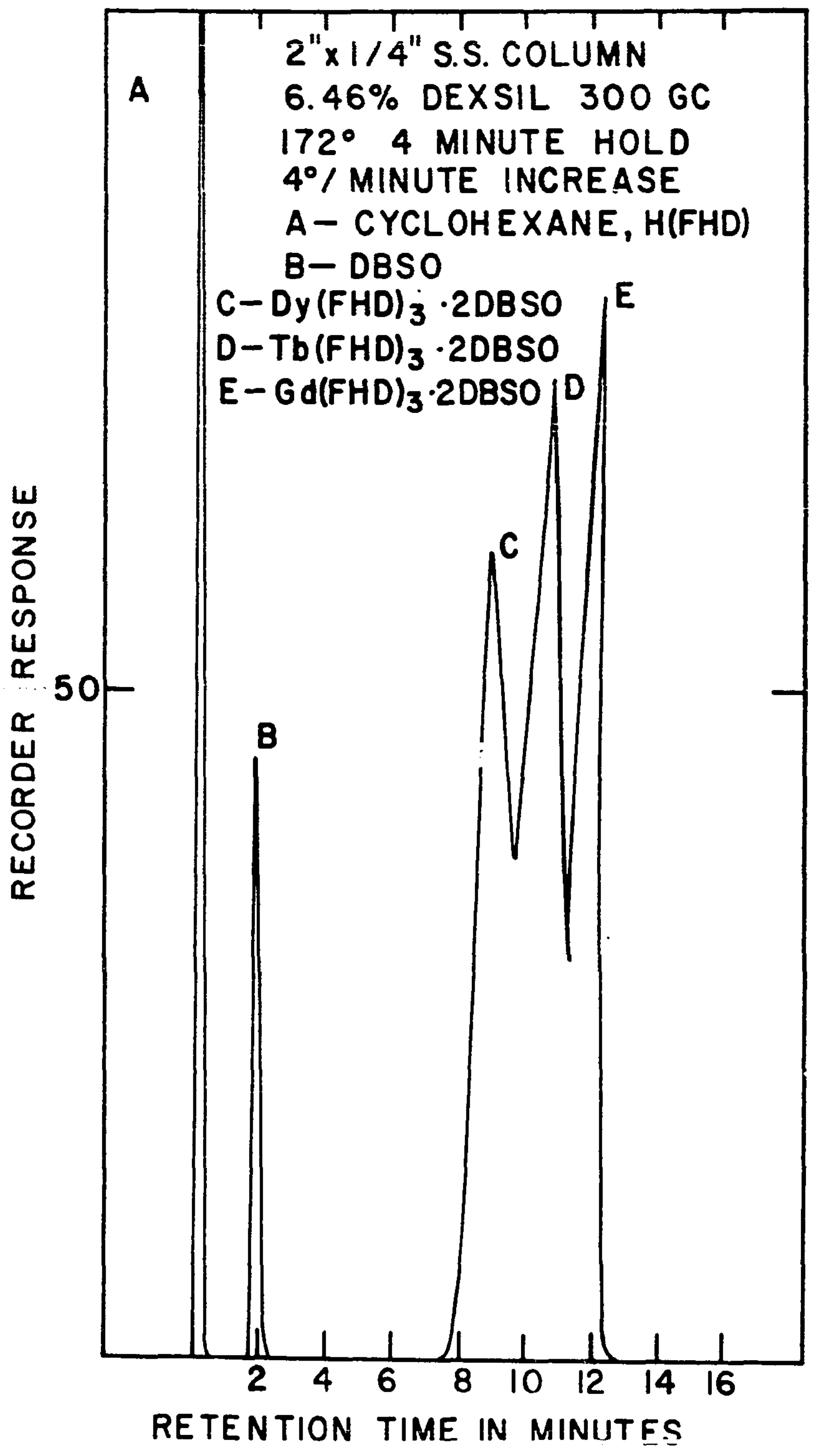


Figure 3.18. Gas chromatogram of a mixture of $Dy(FHD)_3 \cdot 2DBSO$, $Tb(FHD)_3 \cdot 2DBSO$ and $Gd(FHD)_3 \cdot 2DBSO$

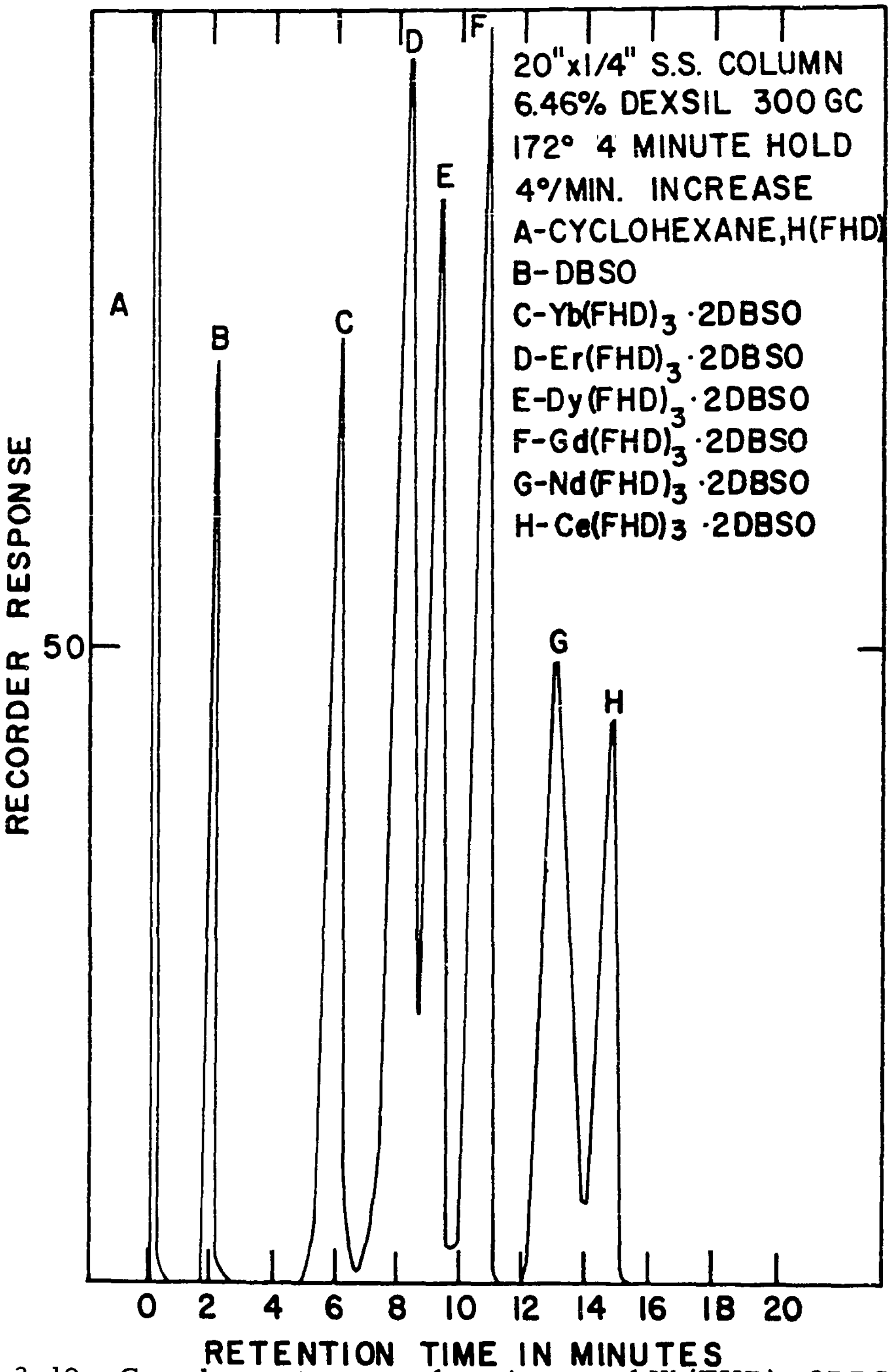


Figure 3. 19. Gas chromatogram of a mixture of $Yb(FHD)_3 \cdot 2DBSO$, $Er(FHD)_3 \cdot 2DBSO$, $Dy(FHD)_3 \cdot 2DBSO$, $Gd(FHD)_3 \cdot 2DBSO$ $Nd(FHD)_3 \cdot 2DBSO$ and $Ce(FHD)_3 \cdot 2DBSO$

The lanthanides commonly exist in ores on an every-other-one basis; therefore, separations on this basis are of high practical utility. The samarium chelate was not included in the mixture to prevent detector swamping caused by the flame enhancement of the samarium chelate. Attempts were made at the separation of a 14 component mixture of the lanthanides, however, only partial resolution was realized.

To achieve quantitative separation of the yttrium group lanthanides a 9.46 % Dexsil 300 GC column was utilized. Figures 3.20 and 3.21 illustrate the separation of several mixtures of the yttrium group lanthanides. Chromatograms for a mixture of ytterbium and gadolinium in different concentration ratios are presented in Figure 3.22. These chromatograms illustrate the excellent separation of the lanthanides when as much as a 10-fold excess of one rare earth is present in the mixture. It should also be noted that at excessively high concentrations the peak shape becomes broader. This broadening is caused by column overloading and is the limiting factor for the upper concentration chromatographable. It was not possible to obtain complete resolution of lutetium, ytterbium and thulium, however qualitative separations could be performed. In all studies, the composition of the eluted species was varified by collection of eluents and subsequent infrared analysis of the trapped samples. The complexes of each metal were eluted without decomposition.

The thermal stability of the FHD-DBSO mixed-ligand system and the separations which could easily be achieved for the lanthanide complexes on the Dexsil 300 GC columns made this system the chromatographic system of choice for use in a quantitative method for

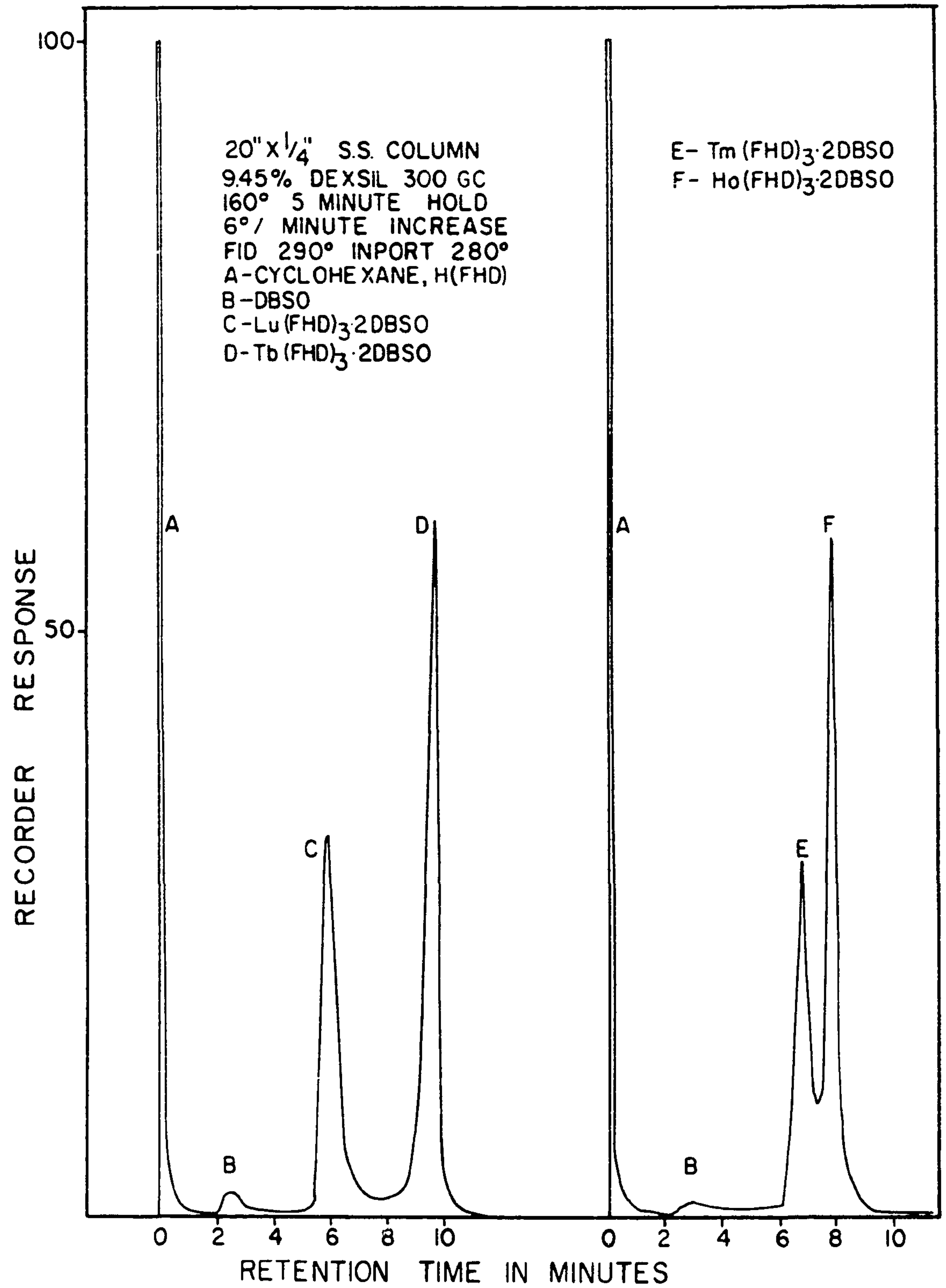


Figure 3.20. Gas chromatograms of mixtures of several lanthanide H(FHD)-DBSO complexes

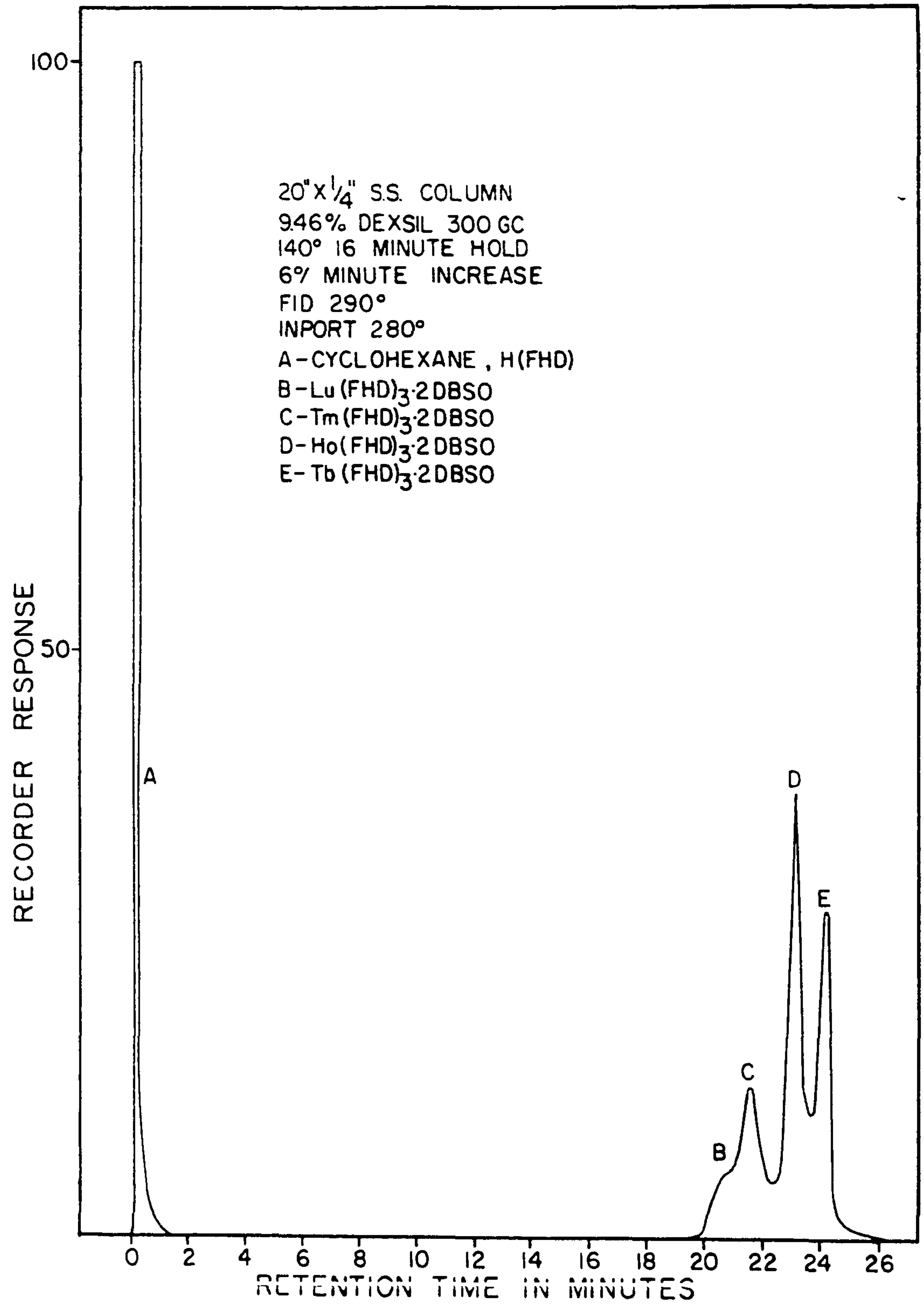


Figure 3.21. Gas chromatogram of a mixture of $Lu(FHD)_3 \cdot 2DBSO$, $Tm(FHD)_3 \cdot 2DBSO$, $Ho(FHD)_3 \cdot 2DBSO_3$ and $Tb(FHD)_3 \cdot 2DBSO$

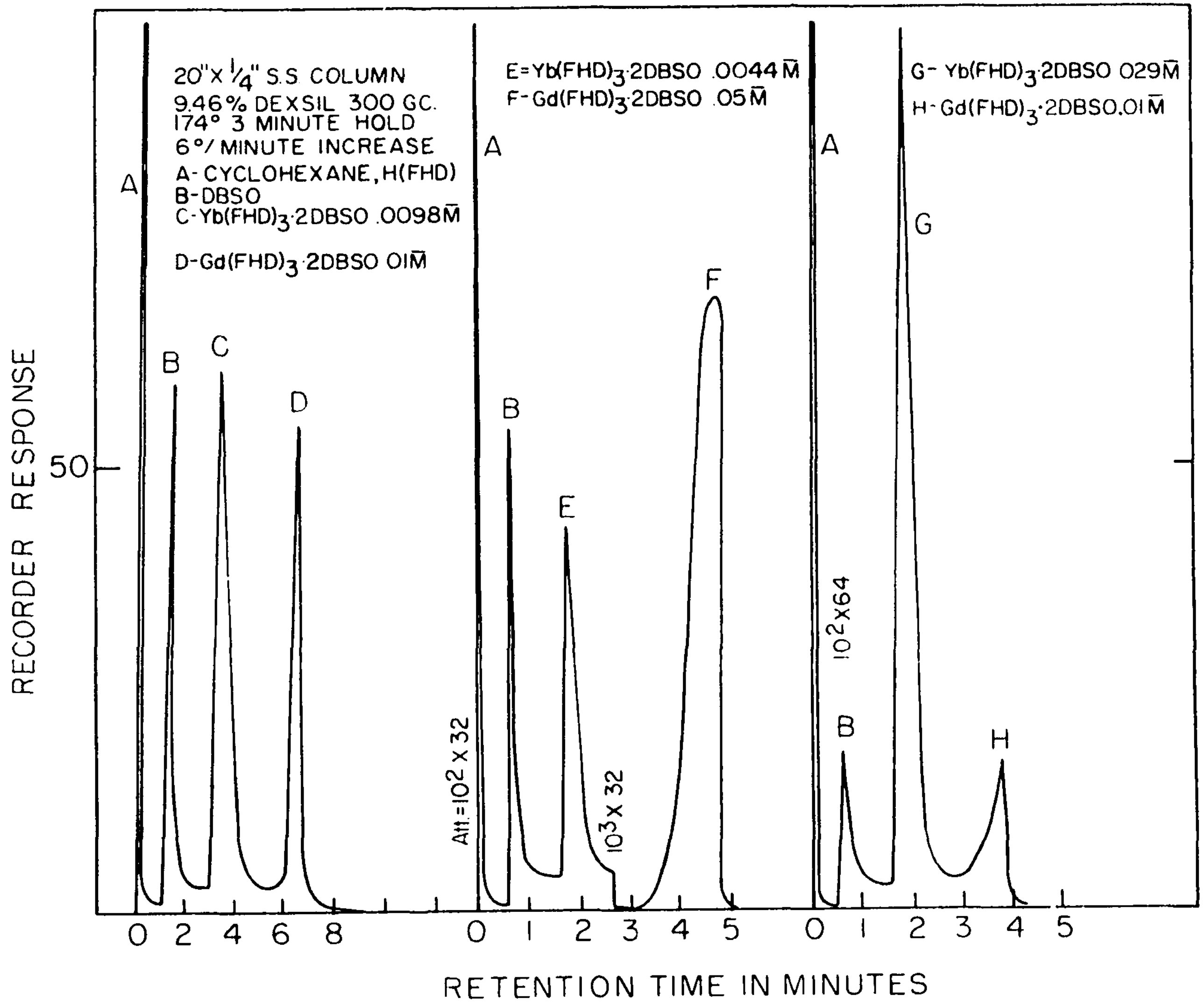


Figure 3.22. Gas chromatogram showing the separation of $Yb(FHD)_3 \cdot 2DBSO$ and $Gd(FHD)_3 \cdot 2DBSO$ in various concentration ratios

the lanthanides.

Calibration curves were prepared for each of the individual lanthanides. The curves were linear over the concentration range 2×10^{-7} to 1.5×10^{-5} g metal. Unknowns were prepared by the same extraction procedure as the standards. To eliminate excess ligand from each extraction, a few milliliters of 0.1 N sodium hydroxide were added to all of the extractions. The H(FHD) forms the insoluble white sodium salt on this treatment. Data for the analysis of the individual lanthanides, using the analytical curves, are presented in Table 3.8. The individual lanthanides were determined with 99.75% recovery with a relative mean deviation of ± 2.60 pph. Calibration curves for mixtures were prepared by using a series of standard solutions containing the lanthanides to be determined in equal concentration ratios. This procedure allows for corrections for peak overlap. Analytical curves for ytterbium and gadolinium are shown in Figure 3.23. The areas of unkowns are indicated by the solid circles. The curves do not extrapolate to zero. This is a result of a finite loss of sample to the column material. Analysis of mixtures of rare earths are given in Table 3.9. The lanthanides were analyzed with 100.24 % recovery and a relative mean deviation of ± 1.78 pph.

Detection limits were determined for all of the rare earths. The detection limit was taken to be that amount of mixed-ligand complex necessary to give a chromatographic peak response equal to or greater than twice the background response. The detection limit observed was 2.0×10^{-7} g metal for all of the rare earths.

The response to the flame ionization detector was found to

Table 3.8. Analysis of the individual lanthanides as H(FHD)-DBSO mixed-ligand complexes

Rare earth	Actual conc. in μgrams	Conc. found in μgrams	Relative error in %
Lu	12.20	11.80	-3.39
	3.86	3.86	0.00
Yb	10.80	10.80	0.00
	3.73	3.89	+4.11
Tm	11.20	10.80	-3.70
	3.84	3.84	0.00
Er	11.70	11.40	-2.63
	3.91	4.09	+4.40
Ho	10.50	10.80	+2.78
	3.48	3.64	+4.39
Dy	10.50	9.97	-5.32
	3.51	3.75	+6.40
Gd	3.49	3.34	-4.49
Tb	10.60	10.80	+1.85
	3.52	3.60	+2.22
Eu	6.38	6.35	-0.47
	3.41	3.44	+0.88
Sm	5.87	5.80	-1.19
	4.44	4.35	-2.03
Pr	4.97	5.04	+1.41
	1.26	1.31	+3.97
Nd	5.72	5.66	-1.05
	3.24	3.20	-1.23
Ce	5.18	5.04	-2.70
	3.16	3.10	-1.90
La	6.47	6.30	-2.63
	4.46	4.08	-4.93

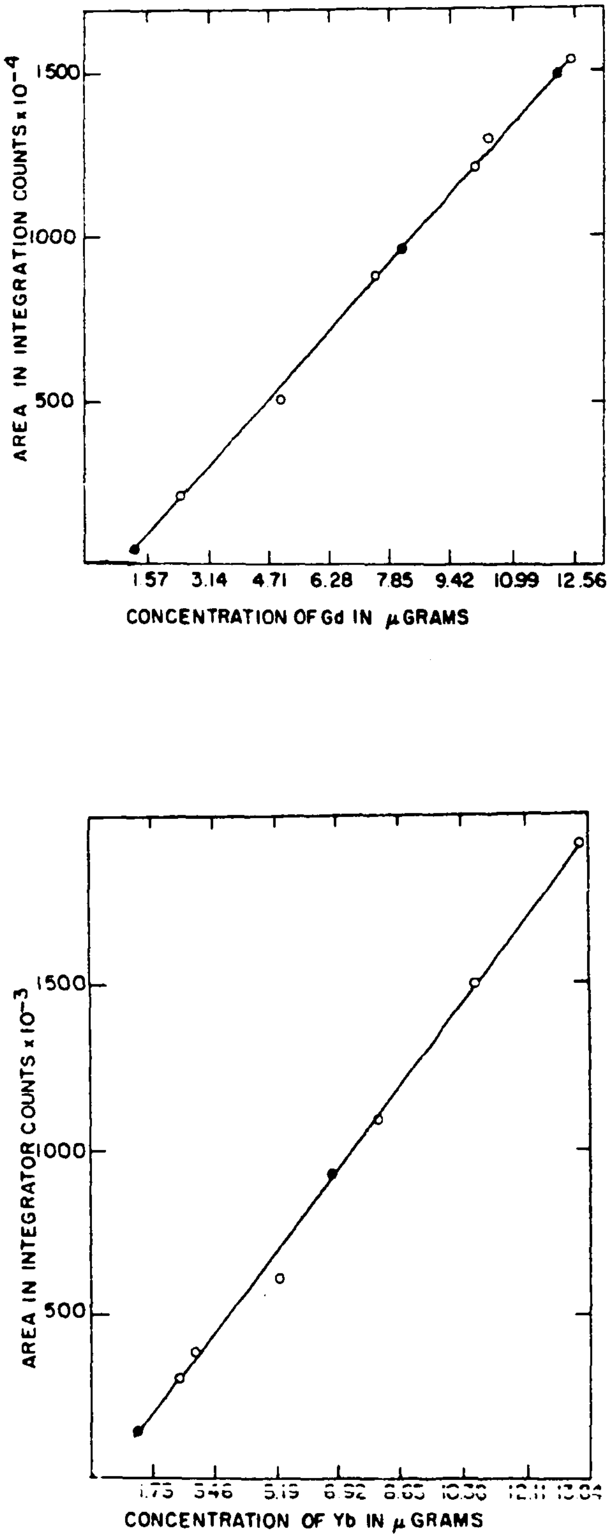


Figure 3.23. Calibration curves for Gd(FHD)$_3$·2DBSO and Yb(FHD)$_3$·2DBSO

Table 3.9. Analysis of mixed rare earth solutions as the H(FHD)-DBSO mixed-ligand complexes

Mixture	Actual conc. in μgrams	Conc. found in μgrams	Relative error in %
Tb	5.28	5.44	+3.03
Lu	5.79	5.96	+2.94
Yb	1.36	1.36	0.00
Gd	12.60	12.20	-3.28
Yb	7.03	6.66	-5.56
Gd	2.52	2.52	0.00
Lu	3.59	3.59	0.00
Dy	3.27	3.31	+1.22
Ho	3.31	3.28	-0.91
Gd	2.66	2.69	+1.13
Eu	10.10	10.10	0.00
Gd	7.05	7.39	+4.82
Sm	2.93	2.96	+1.02
Ce	2.79	2.76	-1.07

vary from metal to metal and is shown in Table 3.10. The variation in response as a function of the metal is probably caused by differences in the combustion of each metal. The extreme enhancement observed when chromatographing the samarium complex limits the usefulness of the method for determining mixtures containing samarium. The detector readily becomes overloaded and may not observe the lower signal from neighboring metal chelates. The response factors are considerably less than those observed with complexes containing TBP as the neutral donor. This is caused by the decrease in number of carbon and hydrogen atoms. The FID responds to the combustion products of hydrocarbon chains, therefore a lower response for the DBSO complexes would be expected.

The mixed-ligand complex of yttrium with H(FHD) and DBSO was easily resolved from all of the lanthanides except erbium and holmium. The relative retention time is very similar to that of erbium so the method is easily extended to the analysis of yttrium.

Mitchell (104) has shown that uranyl, thorium(IV), scandium(III), and iron(III) can be quantitatively separated from the lanthanides by extraction with H(TFA). These metals should not be interferences when removed by prior extraction. Korkisch (82) has summarized several methods for the separation of the lanthanides from all other metals by ion exchange chromatography. Prior separation from major interferences is easily achieved. Although several methods of eliminating interferences are available, the value of an analytical method is increased if the method itself allows for the separation from interferences.

Table 3.10. Response factors for flame ionization detector

Compound	Response factor in integration cnts. x 10^{-5}/μg
$La(FHD)_3 \cdot 2DBSO$	0.28
$Ce(FHD)_3 \cdot 2DBSO$	3.15
$Pr(FHD)_3 \cdot 2DBSO$	1.11
$Nd(FHD)_3 \cdot 2DBSO$	2.15
$Sm(FHD)_3 \cdot 2DBSO$	22.70
$Eu(FHD)_3 \cdot 2DBSO$	4.29
$Gd(FHD)_3 \cdot 2DBSO$	2.72
$Tb(FHD)_3 \cdot 2DBSO$	2.01
$Dy(FHD)_3 \cdot 2DBSO$	4.51
$Ho(FHD)_3 \cdot 2DBSO$	2.57
$Er(FHD)_3 \cdot 2DBSO$	6.52
$Tm(FHD)_3 \cdot 2DBSO$	2.20
$Yb(FHD)_3 \cdot 2DBSO$	0.85
$Lu(FHD)_3 \cdot 2DBSO$	1.80

The utility of the solvent extraction system, as a means for eliminating interferences, was evaluated. Aqueous solutions of the cations, aluminum(III), thorium(IV), iron(III), calcium(II), and uranium(VI), were all prepared and attempts were made at synergistic extraction using H(FHD) and DBSO. Two pH values, 2 and 5.5, were selected for this study. Thorium and uranyl were found to be extracted at both pH 2 and 5.5. Aluminum was 66% extracted at pH 5.5 and not extracted ant pH 2. Iron was extracted at pH 2 but precipitated, as the hydroxide, at pH 5.5. Calcium was not extracted at either pH.

Gas chromatographic analysis of the extracted species in 0.01 $\underline{M}$ erbium solutions containing 0.01 $\underline{M}$ uranyl, thorium, and aluminum indicated that thorium and aluminum did not form an extracted species which competed with the lanthanides for ligands. No peaks were observed for either aluminum or thorium and the elution curve for erbium was identical to that of a chromatogram obtained using a solution containing an equal amount of erbium and no other cations. The extraction of thorium and aluminum apparently does not produce a stable species. Thorium and aluminum, therefore, do not constitute an interference and need not be removed prior to preparation of the lanthanide complexes. Iron(III) and uranium(VI), were found to be interferences when present in equal concentrations with erbium. The extracted iron forms a stable complex which can be chromatographed. The extracted species of uranyl interfered with the extraction of erbium, but did not produce a chromatographic peak. Upon washing with 0.1 N sodium hydroxide both interferences were removed. The iron complex decomposed and precipitated as ferric hydroxide. The uranium complex apparently decomposed also. The techique of sodium hydroxide washing to remove iron chelates from chromatographic extractions is well documented in the literature (130, 131, 132). Evidently this technique is useful in destroying the uranyl extracted species as well.

In summary, an efficient method for the determination of the lanthanides as the mixed-ligand complexes of H(FHD) and DBSO has been developed. This determination offers the first rapid separation and sensitive quantitative method for rare earth analysis. The synergistic extraction system renders the analysis virtually void of interferences and allows the first rapid preparation of volatile and thermally stable lanthanide chelates.

IV. AN INVESTIGATION INTO THE GAS CHROMATOGRAPHIC COLUMN BEHAVIOR OF MIXED-LIGAND COMPLEXES

A. Introduction

This work will describe a study of the columns useful for the gas chromatography of mixed-ligand complexes in regard to the various column interactions and phenomena observed. Several liquid phases were investigated and data are presented to illustrate the nature of the partitioning processes occurring between the lanthanide complexes and the column constituents.

Previous workers (113, 128, 132, 135, 136, 151, 177, 183) have reported unusual adsorption and displacement effects in the gas chromatography of metal chelates. Similar phenomena have been observed during the determination of mixed-ligand complexes by GC and will be reported in the following discussion. A mechanism has been proposed in which the various sources of these non-ideal phenomena are explained.

B. Experimental

1. Apparatus

a. Gas chromatograph A Hewlett-Packard Model 5756B gas chromatograph was used for all column studies. The chromatograms were recorded with a Hewlett-Packard Model 7128A strip chart recorder.

b. Fluorometer Fluorescence data were obtained using an Aminco-Bowman Spectrophotofluorometer equipped with a Mosely X-Y recorder.

2. Reagents and materials

a. Solid supports Chromosorb W-HP, Chromosorb P, Chromosorb W and silanized glass beads were used as supports in these studies and were obtained from Applied Science Laboratories.

b. Liquid phases All liquid phases were obtained from Analabs Inc..

c. Columns Stainless steel columns used were prepared from laboratory stock stainless steel tubing. Glass columns were prepared from Pyrex, borosilicate glass tubing.

d. Solvents All solvents were reagent grade.

3. Techniques

a. Preparation of column packing All column packing was prepared as described in Section III.

b. Packing and conditioning of columns The columns were prepared and conditioned as described in Section III.

c. Silanization of column materials The glass columns were silanized by filling the columns with dichlorodimethylsilane, DCMS, and allowing them to stand over night. The ends of the columns were covered with rubber eyedropper bulbs to prevent evaporation. After the DCMS was drained from the columns they were air dried using a gentle flow of filtered air.

The chromosorb W was silanized by placing the coated support in a screw cap jar. The jar was then filled with DCMS until the surface of the solid support was completely submerged. The jar was closed and allowed to stand for one hour. The slurry was then placed in a 2 inch x.10 inch cylindrical tube fitted with a glass frit. The DCMS was drained from the support through a stopcock below the glass frit. Filtered air was passed through the packing while heat was applied by infrared lamps.

d. Sample collection Samples were collected, as eluted from the gas chromatograph, in glass collection traps in which a ball of glass wool had been placed. The collection traps were placed at the exit end of the column and air cooled to room temperature. The collected samples were then washed from the trap with a solvent suitable for subsequent analysis.

4. Analytical determinations

a. Determination of silicone liquid phases The weight percentage of liquid phase for silicone polymer type supports can not be determined by burning off the liquid, because of the formation of silicon dioxide. The amount of immobile support was determined by placing a weighed amount of packing in a ten milliliter ion exchange column plugged with glass wool and subsequent washing of the packing with copious amounts of the solvent used to dissolve the liquid phase. The percentage of silicon coating was then calculated as follows:

$$\%\ \text{liquid coating} = \frac{\text{g column packing} - \text{g support after washing} \times 100}{\text{g column packing}}$$

c. Identification of eluted species Complexes of europium and terbium were identified by comparison of the apparent fluorescence of samples eluted from the gas chromatographic column with that of the organic phase of the extraction.

C. Results and Discussion

1. Partitioning of mixed-ligand complexes with various liquid phases

The majority of the work done on the determination of metal complexes by GC has been performed with columns utilizing silicon or fluorosilicon liquid phases (25, 60, 61, 69, 95, 109, 110, 130, 132, 135, 136, 140, 142, 146, 158, 163, 167, 171, 173, 174, 192).

The hydrocarbon type liquid phases such as Apiezon greases were not found to be very satisfactory (46, 61, 183). Recently Sieck (151) has reported a complete study of the various types of liquid phases including the porous polymer supports, Porapak Q and Porapak T.

The early work done on the determination of metal complexes by GC found the wide application of lightly loaded columns but most of the recent studies including the majority of those listed above have used 2 to 10 % liquid loadings. The use of the high loadings has enabled the realization of better partitioning and better resolution but has added new partitioning phenomena.

To be suitable for use in the determination of the lanthanides by gas chromatography the liquid phase must possess a high thermal stability. This requirement of high thermal stability eliminates all but a few of the currently available liquid phases. The phases used for this study were SE-30, a polysiloxane liquid with methyl substituents, QF-1, a polysiloxane liquid with methyl and 1, 1, 1-trifluoropropyl substituents, and Dexsil 300 GC, a carborane cage compound, cross linked by methyl substituted polysiloxane chains.

To determine the partition ratio for the lanthanides with each phase a series of ten columns of 20 inch x 0.25 inch o.d. stainless steel was prepared. The packing used ranged from 0 to 25 % w/w liquid phase. The partition ratio was determined using Equation 3.8

and plotted versus the weight of liquid phase in the column. The mixed-ligand complex of terbium with H(FHD) and DBSO was selected for study for two reasons; the complex fluoresces intensely, so eluents can be identified and terbium lies in the middle of the lanthanide series so its column behavior should be intermediate between the extremely volatile and less volatile limits. The chromatographic conditions of carrier flow, detector temperature and column temperature were all held constant at 50 ml/min helium, 290°C FID and 200° C respectively. Methane was used to determine the value of t_{r_o}.

Figure 4.1 presents the partition ratio for the terbium complex as a function of the weight of liquid phase present for SE-30, QF-1 and Dexsil 300 GC columns. The linear variation of partition ratio with the amount of liquid phase indicates that gas-liquid partitioning is occurring between the mixed-ligand complexes and the liquid phases used. The similarity in partitioning observed with Dexsil 300 GC and SE-30 is a result of the similarity in polarity of the two phases.

The partitioning is greater with QF-1 than with either SE-30 or Dexsil 300 GC. This increased partitioning is a result of the increased polarity of QF-1. QF-1, a phase of intermediate polarity, would be expected to interact to a higher degree with the polar DBSO containing complex than would either of the non-polar phases SE-30 and Dexsil 300 GC.

All curves have a non-zero intercept, which terminate at the same value, that of the partition ratio observed with no liquid phase present. Veening and Huber (183) have suggested that this observation indicates some of the complex is retained by the solid

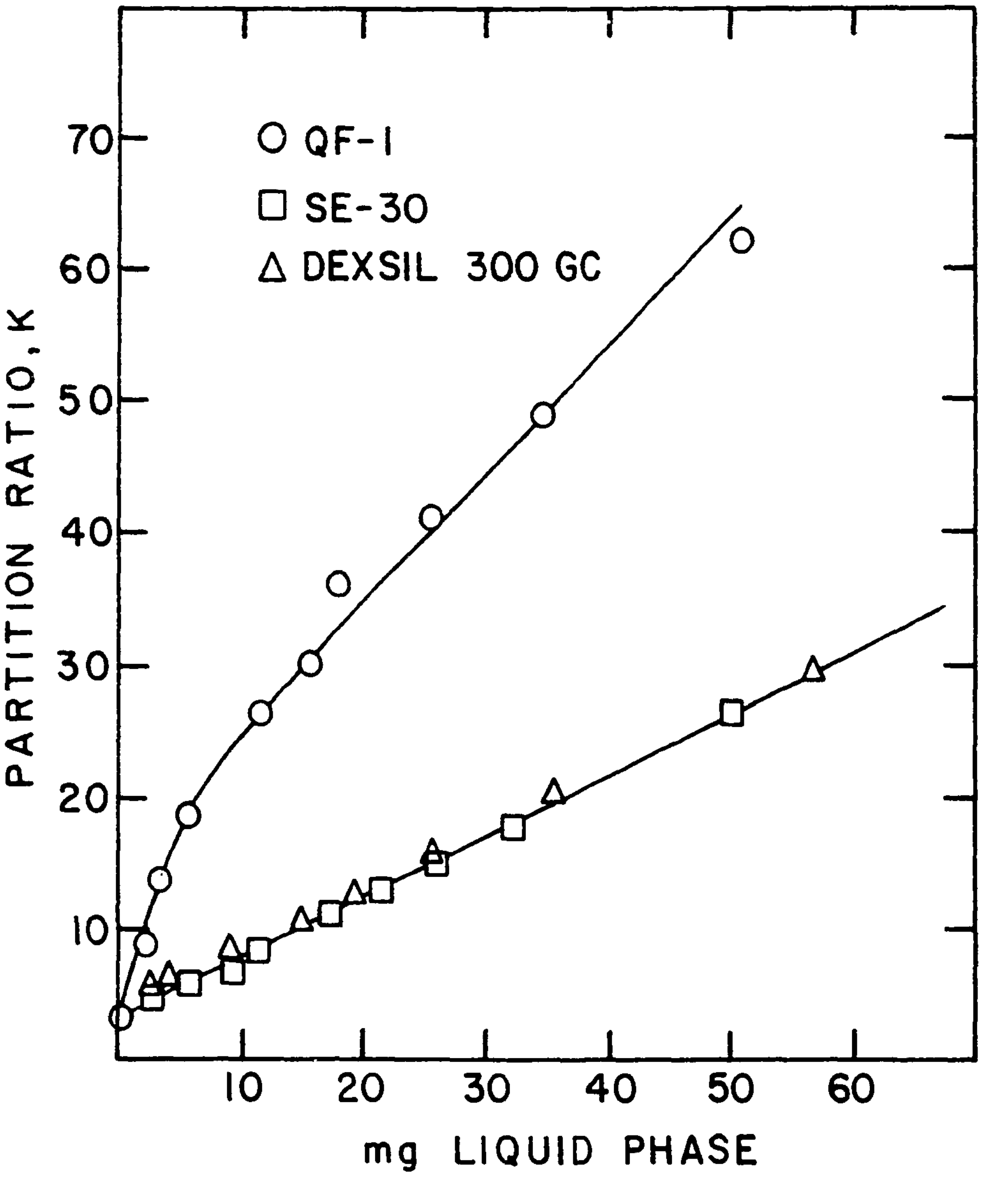


Figure 4.1. Graph of the partition ratio, K, as a function of mg liquid phase present

support used in the GLC column. If only gas-liquid partitioning were occurring, a zero intercept would be anticipated for these plots. Other workers (151, 183) have extrapolated to 0.0 g liquid phase loading, having only accumulated data at three or four points in the higher liquid phase concentration range. The plot for QF-1 shows that this procedure is invalid and could lead to the erroneous conclusion that the solid support has a greater effect on partitioning, than is actually the case. It is an extremely risky practice to attribute solid adsorption to a condition which may be a manifestation of a volatility difference between the complex and an unretained solute.

To ascertain whether or not actual adsorption on the solid surface was occurring, two additional columns, both 20 inch x 0.25 inch stainless steel, were prepared. The first was packed with 100/120 mesh silanized glass beads and the second was packed with 100/120 mesh Chromosorb P. The silanized glass beads should be totally inert to adsorption and the Chromosorb consisting of ground fire brick, is a very active adsorbent. The conditions of flow and temperature were held constant at 50 ml/min helium and 200 °C.

Chromatograms were obtained for $Tb(FHD)_3 \cdot 2DBSO$ on both of these columns and the partition ratio, $\underline{k}$, was calculated. The calculated ratios for all three uncoated supports are given in Table 4.1. It is apparent from these data that it is not valid to assume that a non-zero intercept for a $\underline{k}$ vs mg phase plot indicates the total extent of solid surface partitioning. If this assumption were valid the $\underline{k}$ value for the glass beads should be the lowest. The high $\underline{k}$ value for the glass beads is probably a result of the more efficient packing

Table 4.1. Partition ratios for $Tb(FHD)_3 \cdot 2DBSO$ on various uncoated supports

Support	k
100/120 mesh Chromosorb W-HP	3.5
100/120 mesh Silanized glass beads	14.4
100/120 mesh Chromosorb P	17.5

realized by the glass beads. This tight packing creates a distillation column of a great number of theoretical plates. The boiling point difference between the complex and methane causes an apparent increase in partitioning of the chelate.

The difference in partition ratio for the Chromosorb P and Chromosorb W-HP is a result of increased adsorption on the Chromosorb P, since both of these supports should pack similarly. The partitioning observed with the Chromosorb W-HP is not totally a result of solid adsorption. Volatility differences between the chelates and the unretained solute may increase the observed value. The *k* observed is the maximum value possible as a result of adsorption on the solid support. To obtain accurate assignment of partitioning caused by solid adsorption, a non-retained solute of similar volatility to the compound of interest must be used. This corrects for apparent partitioning caused by volatility differences.

The plot for partitioning on QF-1 would extrapolate to a higher *k* value than that observed on bare support. This additional contribution to the partitioning is a result of adsorption on the liquid surface.

The point of inflection for this plot occurs at approximately 5 mg of QF-1, which for this column corresponds to a 2% coated column. Craig (32) has determined that at this point the surface of the solid support is completely covered. Evidently at loadings less than 2% the effect of solid surface adsorption begins to predominate at the loss of bulk liquid partitioning and liquid surface adsorption.

For QF-1 columns at least three phenomena must be contributing to the retention volume; (i) bulk partitioning with the liquid phase, KV_L; (ii) adsorption on the solid support, k_sA_s; and (iii) adsorption on the surface of the liquid phase, k_aA_L. For the SE-30 and Dexsil 300 GC columns the net retention volume of the mixed-ligand complexes is apparently a function only of the partitioning behavior of the complex with the liquid phase, KV_L, and adsorption by the solid support, k_sA_s.

It is also possible that interaction with the bulk liquid by complexation or other forms of association may make an appreciable contribution to the retention observed when QF-1 is used as the liquid phase. This type of interaction is likely to occur when polar liquid phases are used and polar solutes chromatographed. Experimentally this results in chromatographic peaks which have sharp leading edges with long tailing edges (31). As shown in Figure 4.2 this peak asymmetry is observed when QF-1 columns are used but not when Dexsil 300 GC columns are used. Other non-equilibrium phenomena such as loading of coordination sites on the column, displacement of previously studied complexes and elution of complexes containing liquid phase should be observed if this association is occurring. Such phenomena have been observed and will be discussed in the following

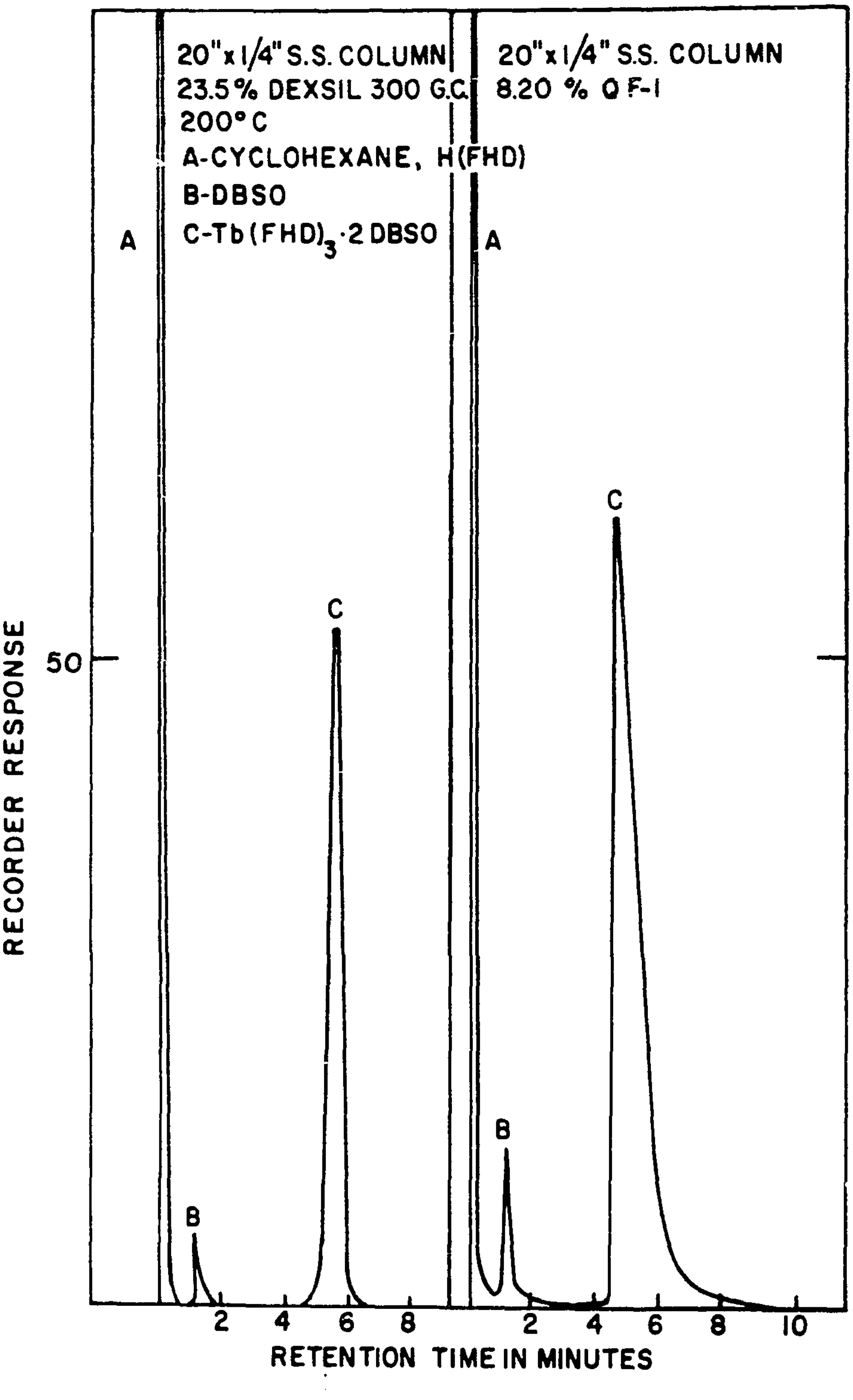


Figure 4.2. Gas chromatograms for Tb(FHD)$_3$·2DBSO on columns containing Dexsil 300 GC and QF-1 as liquid phases

section.

2. Loading, displacement and other non-ideal column behavior of mixed-ligand complexes

With the exception of chromium and berylium, the quality of gas chromatography reported for metal diketonates is poorer than that of organic compounds of comparable volatility. Chromatographic peak shapes obtained are often asymmetric with many anomalous shoulders and other extraneous peaks, and evidence of interaction with the column packing is often apparent.

One of the most frequently reported observations in the study of metal diketonates has been the requirement of injections of a particular diketonate to "load" the column before peaks of consistent size and shape appear, indicating that adsorption sites are being deactivated (113, 128, 132, 135, 136, 151, 177, 183). The situation becomes more complicated for mixtures of metal chelates, where a sequence of adsorption, displacements and possibly further interaction and breakdown is involved.

To determine which columns would be most suitable for the chromatography of mixed-ligand complexes, nine 20 inch x 0.25 inch stainless steel columns of Dexsil 300 GC, SE-30 and QF-1 were prepared in the phase range of 0.0 to 25 % w/w. By maintaining the flow rate and all other parameters constant and monitoring the precise history of the columns, the "loading" of each column was determined. Small sample volumes, 0.2µl or less, of 0.01 M $Tb(FHD)_3 \cdot 2DBSO$ were injected into the chromatograph and elution of the chelates was determined by FID response. Assuming that the loading is additive, the amount of complex required before elution occurred was determined and plotted vs the mg liquid phase present. In this manner the effect of the type and amount of liquid phase on the "loading" could easily be evaluated. The results of this experiment are shown in Figure 4.3. For the liquid phases QF-1 and SE-30 the loading increases as the amount of liquid phase increases. The Dexsil 300 GC liquid phase apparently has the least loading of all phases. The loading for the Dexsil 300 GC columns is nearly constant with that observed with only solid support present. All of the curves extrapolate to the loading observed with no liquid phase present.

Previous workers (151, 177) have attributed the loading to adsorption on active sites on the solid support. If this were the case the loading should be constant or diminish as the surface is covered by the liquid phase. This is not observed, except with the Dexsil 300 GC columns, therefore another mechanism must be proposed.

The loading may be occurring by non-equilibrium association or complexation with the liquid phase. As shown in Figure 4.3 the loading is highest with the polar liquid phase, QF-1. The polarity of the liquid phase should enhance association with the polar complexes. If the association occurs within the liquid phase, an increase in loading should be found as the amount of liquid phase increases. With the columns containing QF-1 an increase of this type is observed.

The liquid phase SE-30 also possess an appreciable loading. This loading is less than that observed when QF-1 columns were studied. The decrease in loading is a result of a decrease in polarity of the liquid phase. The less polar phase would be expected to interact

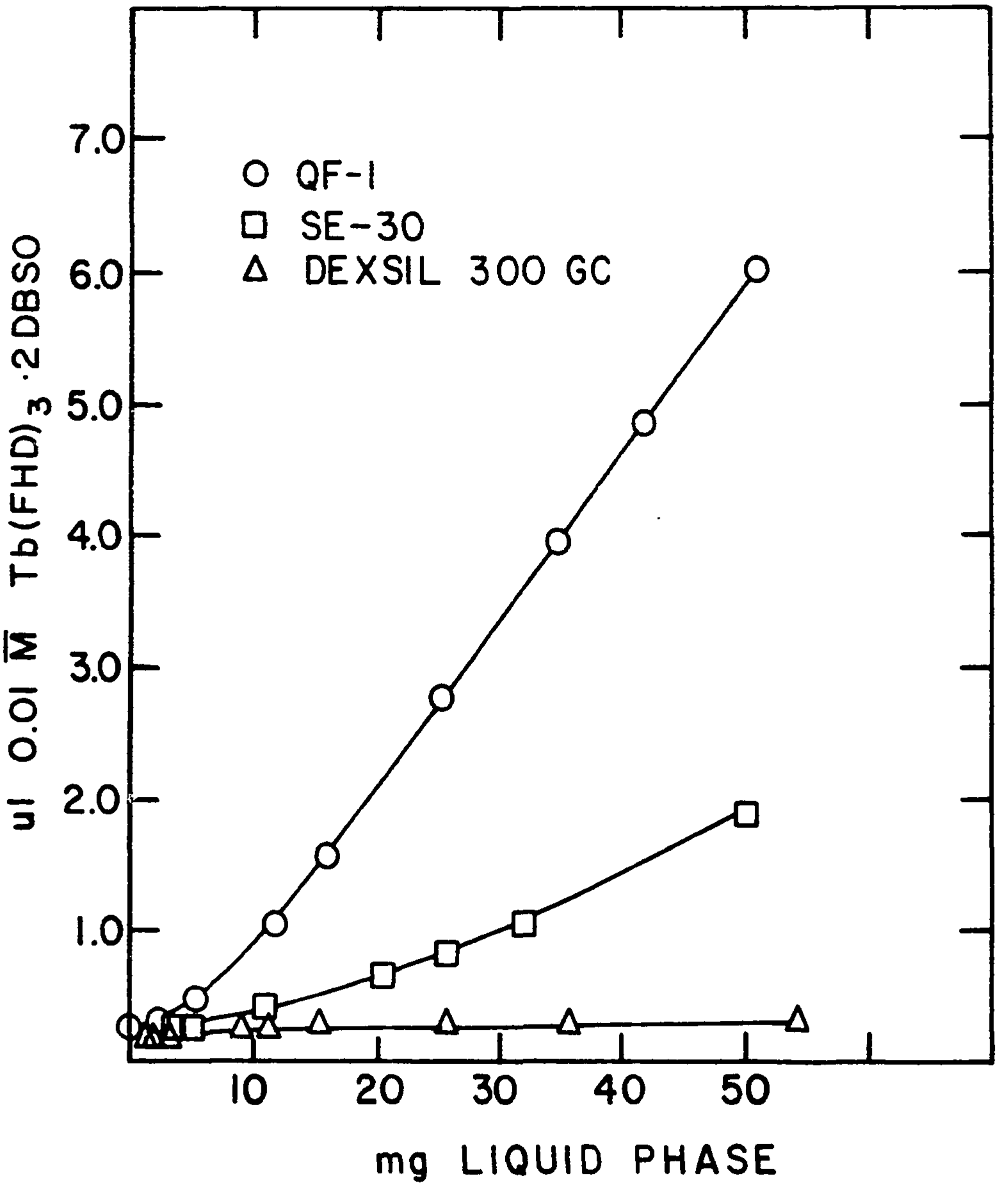


Figure 4.3. Loading of $Tb(FHD)_3 \cdot 2DBSO$ as a function of mg liquid phase present

less strongly with a polar solute. The loading does increase as the amount of SE-30 in the column increases. As with the QF-1 columns the increase indicates association or complexation with the liquid phase. Increase polarity enhances this interaction as does increased liquid phase thickness. Uden and Jenkins (177) have reported adsorption with polar liquid phases even on Teflon supports. In certain cases with polar phases they were unable to achieve elution of any chelates.

Dexsil 300 GC is both structurally similar, with the exception of the meta-dicarboclovododecaborane cage units, and equal in polarity with SE-30. On this basis the loading should be similar. As shown in Figure 4.3 the loading on Dexsil 300 GC does not increase as amount of liquid phase increases. The loading remains constant at the level observed for bare Chromosorb W-HP. Evidently the carborane cages either offer steric interference to the interaction with the liquid phase or affect the manner in which the liquid phase is laid down on the support in such a way as to prevent association with highly oriented layers.

The solid support also makes a contribution to the loading. Evidence for solid support interaction is the constant loading of the Dexsil 300 GC columns. Furthermore, experiments with columns containing uncoated glass beads gave no indication of column loading. As the amount of liquid phase completely covers the solid support the active sites on the support should be covered and thereby be prevented from interaction. Keller (80), however, has determined that even at 30 % liquid phase the solute theoretically has time to reach the solid surface. Since the solute can reach the surface under the chromatographic conditions described, interaction and loading at this surface can occur.

Apparently the loading is a multiple process which depends on the solid support, the polarity and structure of the liquid phase and the nature of the complex.

Displacement of previously determined complexes by other metal complexes has also been observed. Columns containing QF-1 and SE-30 were found to exhibit this phenomena. The displacement of europium by terbium could be observed by monitoring the apparent fluorescence of trappings from a column loaded with europium. Figure 4.4 shows the apparent fluorescence spectrum for $Tb(FHD)_3 \cdot 2DBSO$ and Figure 4.5 shows the apparent fluorescence spectrum for $Eu(FHD)_3 \cdot 2DBSO$. The apparent fluorescence spectra for samples of $Tb(FHD)_3 \cdot 2DBSO$ collected as eluted from the chromatographic column are shown in Figure 4.6. These samples were chromatographed after several determinations of $Eu(FHD)_3 \cdot 2DBSO$ on the SE-30 column. The chelate exchange is obvious as the intensity of the fluorescence of terbium increases while the intensity of europium fluorescence decreases. This exchange is quantitative as shown in Figure 4.7. When the displacement behavior is observed chromatographically, the peaks have the same retention times as the individual comlexes. The constant retention time is explained if a uniform loading of the initial chelate occurs throughout the column. As the second chelate starts through the column some of the previously loaded chelate is displaced. This displacement begins at the inport end of the

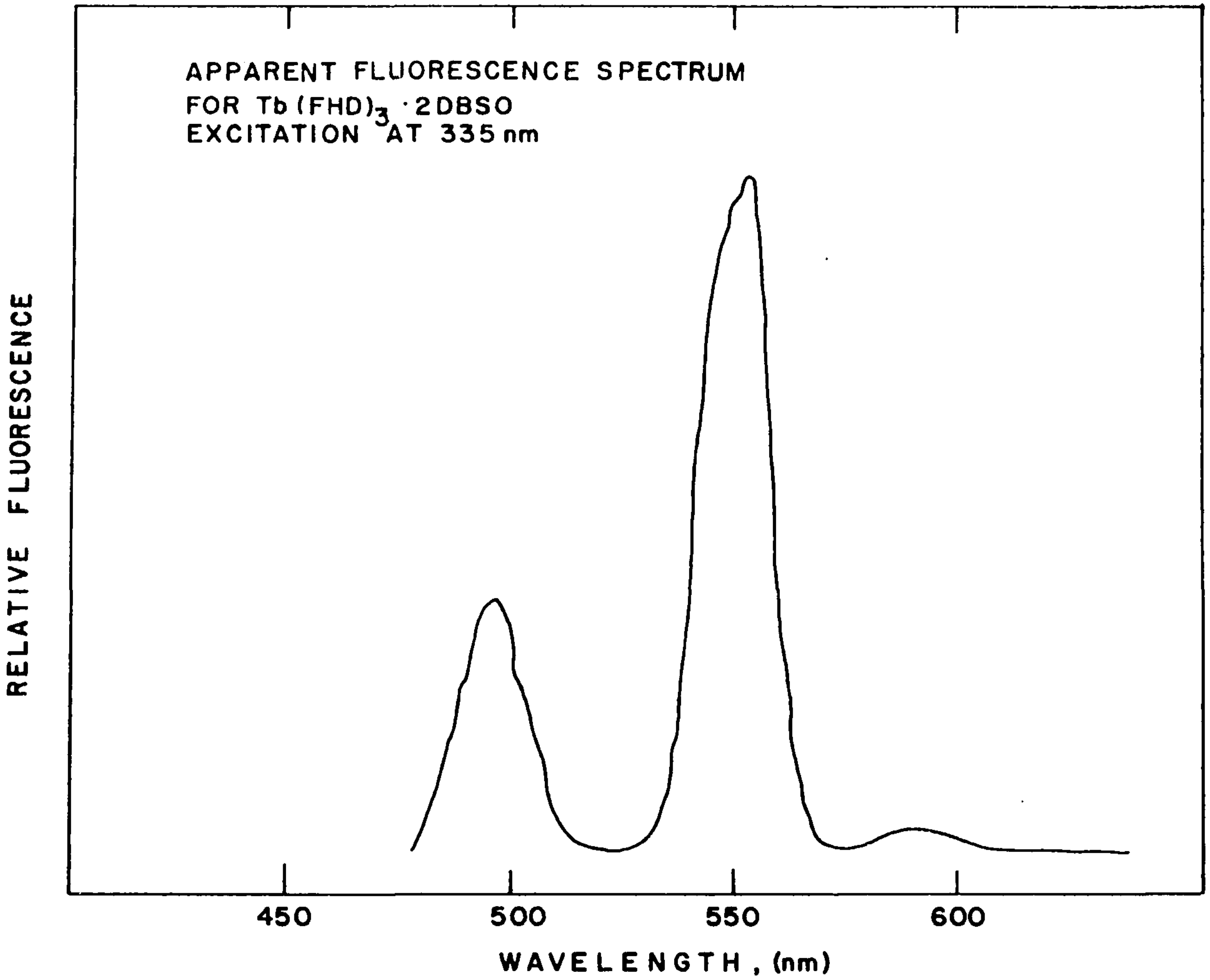


Figure 4.4. The apparent fluorescence spectrum for Tb(FHD)$_3$ · 2DBSO

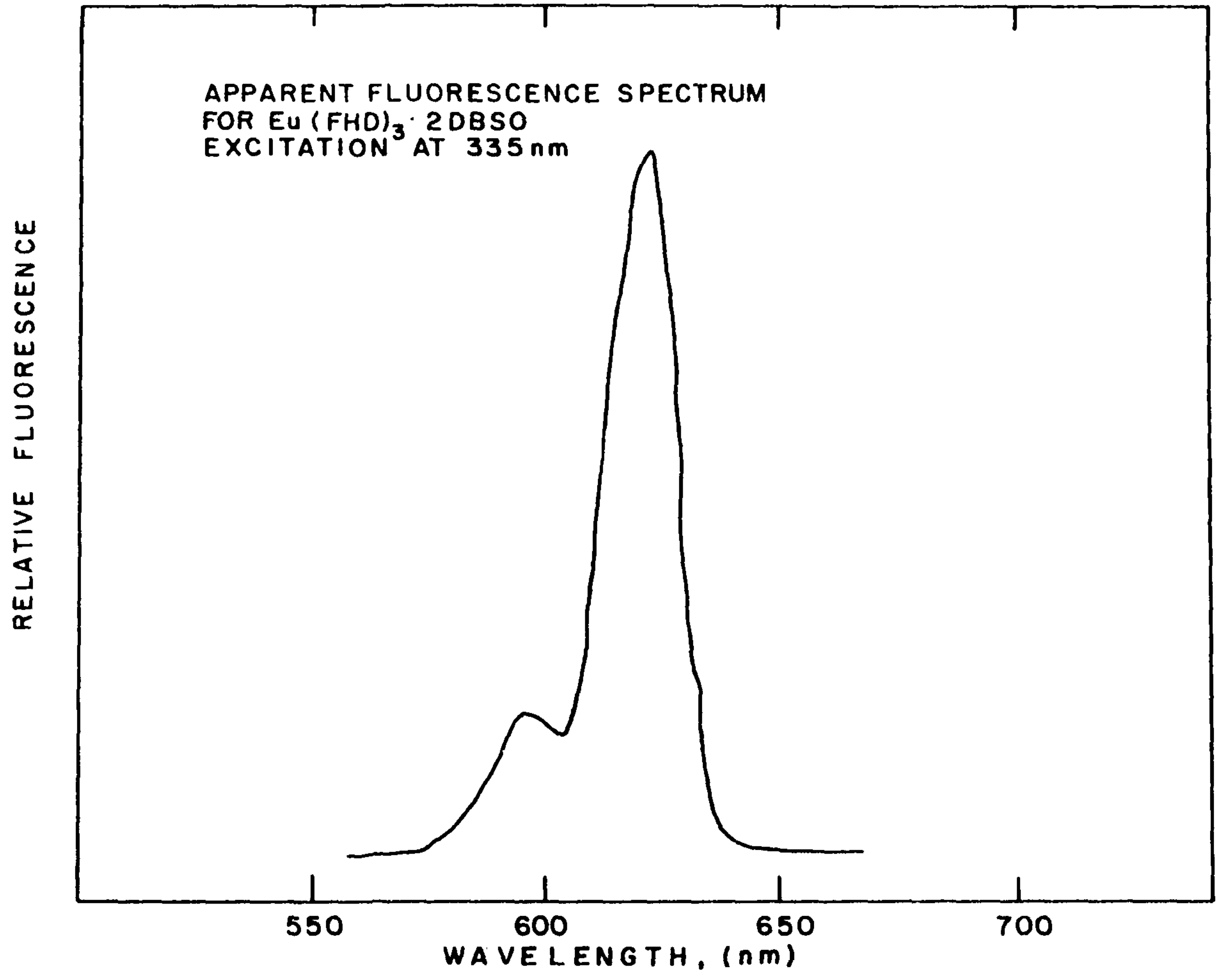


Figure 4.5. The apparent fluorescence spectrum for Eu(FHD)$_3$·2DBSO

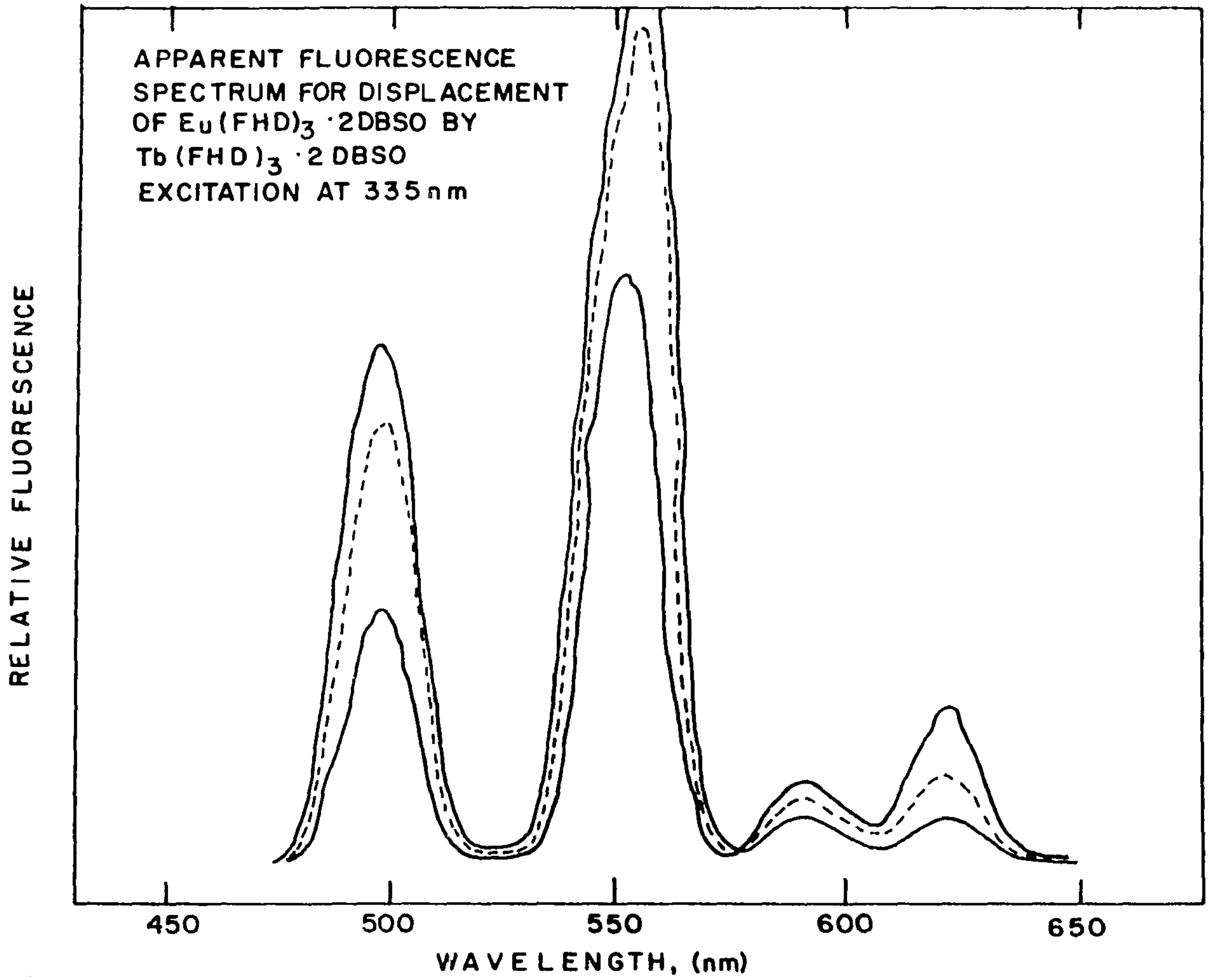


Figure 4.6. The apparent fluorescence spectra for $Eu(FHD)_3 \cdot 2DBSO$ and $Tb(FHD)_3 \cdot 2DBSO$ taken from trappings of chromatographic eluents

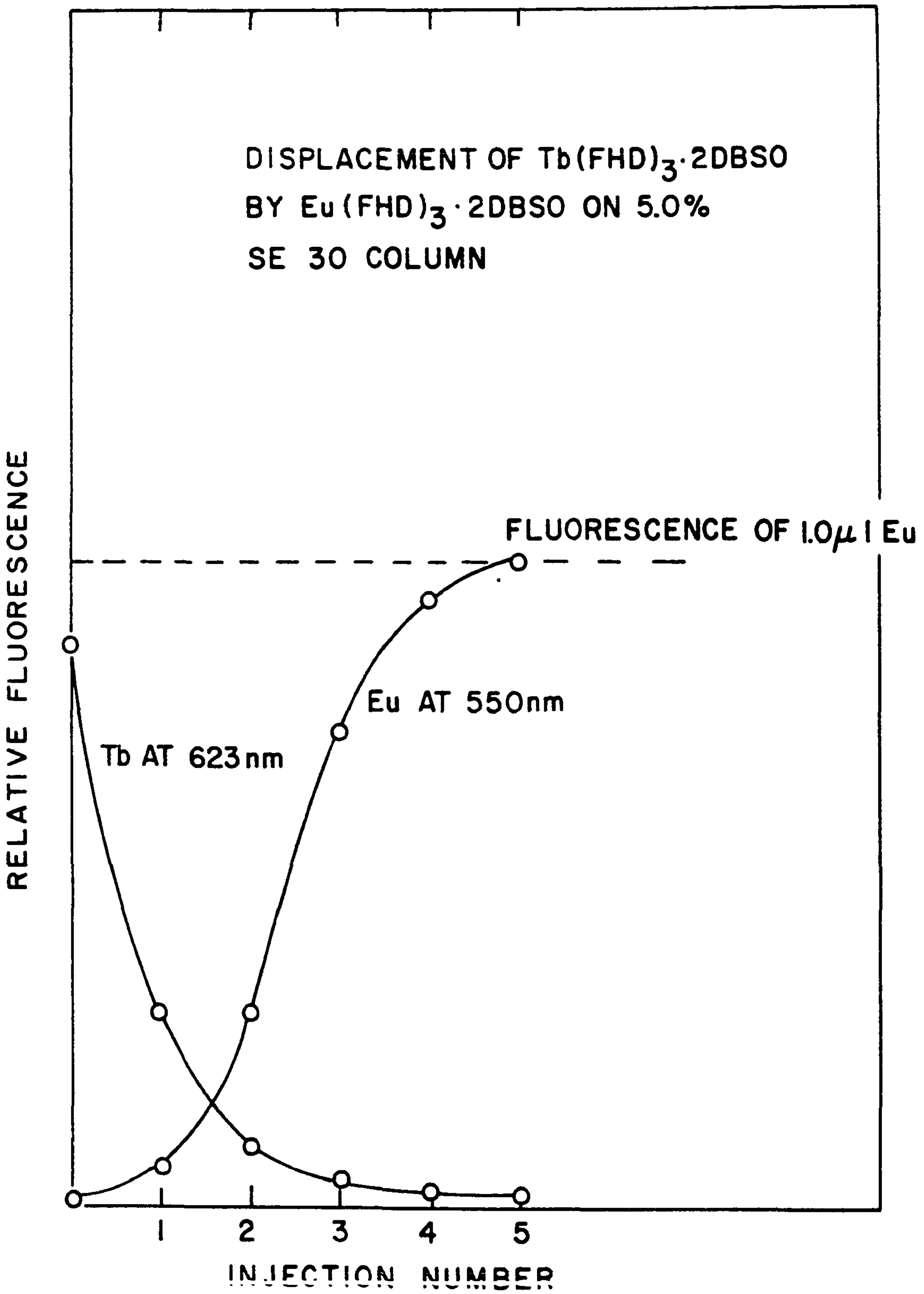


Figure 4.7. Displacement of $Tb(FHD)_3 \cdot 2DBSO$ by $Eu(FHD)_3 \cdot 2DBSO$ as determined by fluorescence analysis of gas chromatographic eluents

column, then both complexes move down the column and are partitioned. Eventually all of the previously loaded complex is displaced (after several injections) and the column performs quantitatively for the new complex. This displacement interaction is particularly bad when polar liquid phases are used and has been observed even with Teflon solid supports (177).

Columns packed with Dexsil 300 GC were not found to exhibit this displacement phenomenon. This suggests that the displacement is related to the loading occurring on and/or in the liquid phase and not the loading on the solid surface.

The interaction with the solid surface has been reported to be a result of active hydroxyl groups present in the support material. Uden and Jenkins (177) suggested silanizing the solid support to eliminate these active hydroxyl groups. To assess the value of this technique four, 4 foot x 0.25 inch glass columns were prepared in various states of silanization. These columns are listed in Table 4.2. Column number one was used as a control column and demonstrated the loading and displacements discussed above. All columns which had been silanized demonstrated unsatisfactory chromatographic behavior. Column number three showed the greatest loading and displacement phenomena of all the columns studied. Column number four also showed extensive loading. Chromatograms obtained when columns three and four were used contained may spurious peaks and the retention times of the complexes were observed to decrease after several days of use. Apparently the silanization of columns and/or column packing material produces a detrimental effect on the elution of

Table 4.2. Gas chromatographic columns used to determine the effect of silanization

1. glass, 5.0 % SE-30 on Chromosorb W
2. silanized glass, 5.0 % SE-30 on Chromosorb W
3. silanized glass, 5.0 % SE-30 on silanized Chromosorb W
4. glass, 5.0 % SE-30 on silanized Chromosorb W

mixed-ligand complexes of the lanthanides and should not be done. This decrease in column performance on silanization suggests that the interactions may be occurring with the silicone polymers themselves.

The last phenomenon observed is that of spurious peaks and shoulders. This phenomenon was noted in the studies utilizing QF-1 and SE-30 and is shown in Figure 4.8. Qualitative identification , by eye observation, confirmed the presence of lanthanide in the extraneous peaks (the flame in the FID burned red, the characteristic color of the diketonate). Attempts at fluorescence analysis of trappings of the peaks failed to confirm the presence of complex. It is possible that some chelate decomposition or ligand exchange is occurring in the bulk liquid. If this were the case injections of H(FHD) and DBSO, either singly or mixed, immediately following elution of chelates, should result in reformation of the complex and subsequent elution. When these experiments were tried no elution of complex was observed. Uden (177) also encountered this problem and successfully utilized mass spectral analysis to identify the peak composition for iron TFA complexes. They report the composition to be the same as the injected chelate with the exception of traces of SE-30 bleed. Other workers

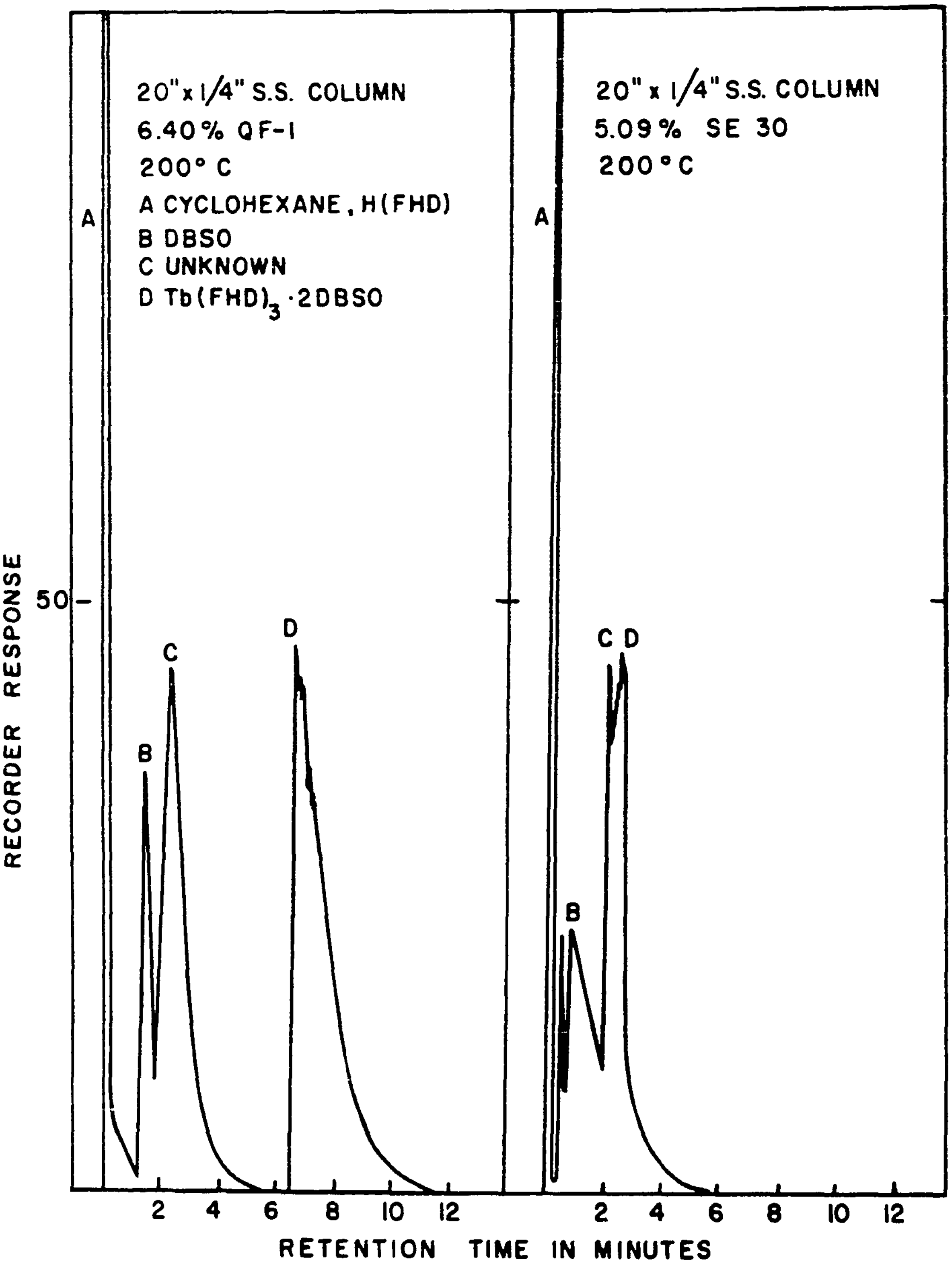


Figure 4.8. Gas chromatograms for $Tb(FHD)_3 \cdot 2DBSO$ on SE-30 and QF-1 columns

have reported this type of interaction with gallium and indium TFA complexes (143).

These results show that when QF-1 and SE-30 are used as the liquid phase for metal chromatography. care must be taken before retention times are reported. Particularly the history and age of the columns should be known as older columns may have less liquid phase.

No spurious peaks were observed in studies utilizing Dexsil 300 GC as liquid phase. Apparently the nature of this interaction is also liquid phase dependent and not solid surface controlled.

These non-equilibrium interactions have not been reported for the totally inert chromium complex. It is possible that the lack of interaction is a result of the inertness of the complex; since an inert complex would not be expected to associate with the liquid phase. If other inert complexes were prepared they too should be void of these interactions.

To test this proposition H(FHD) and DBSO complexes of iron, cobalt and nickel were prepared. No attempt was made at determining the stoichiometry of these complexes. Each complex was successfully eluted from a QF-1 column as shown in Figure 4.9. No non-ideal effects were observed even with the iron complex which has been shown to undergo severe non-ideal interaction when chromatographed as other diketonato complexes. This stability and excellent chromatographability is a manifestation of both the ligand H(FHD) and the successful total coordination by the use of a mixed-ligand system.

In summary, the retention behavior observed with mixed-ligand chelates includes contributions from partitioning on the solid surface, and with the bulk liquid. When polar liquid phases such as QF-1 are

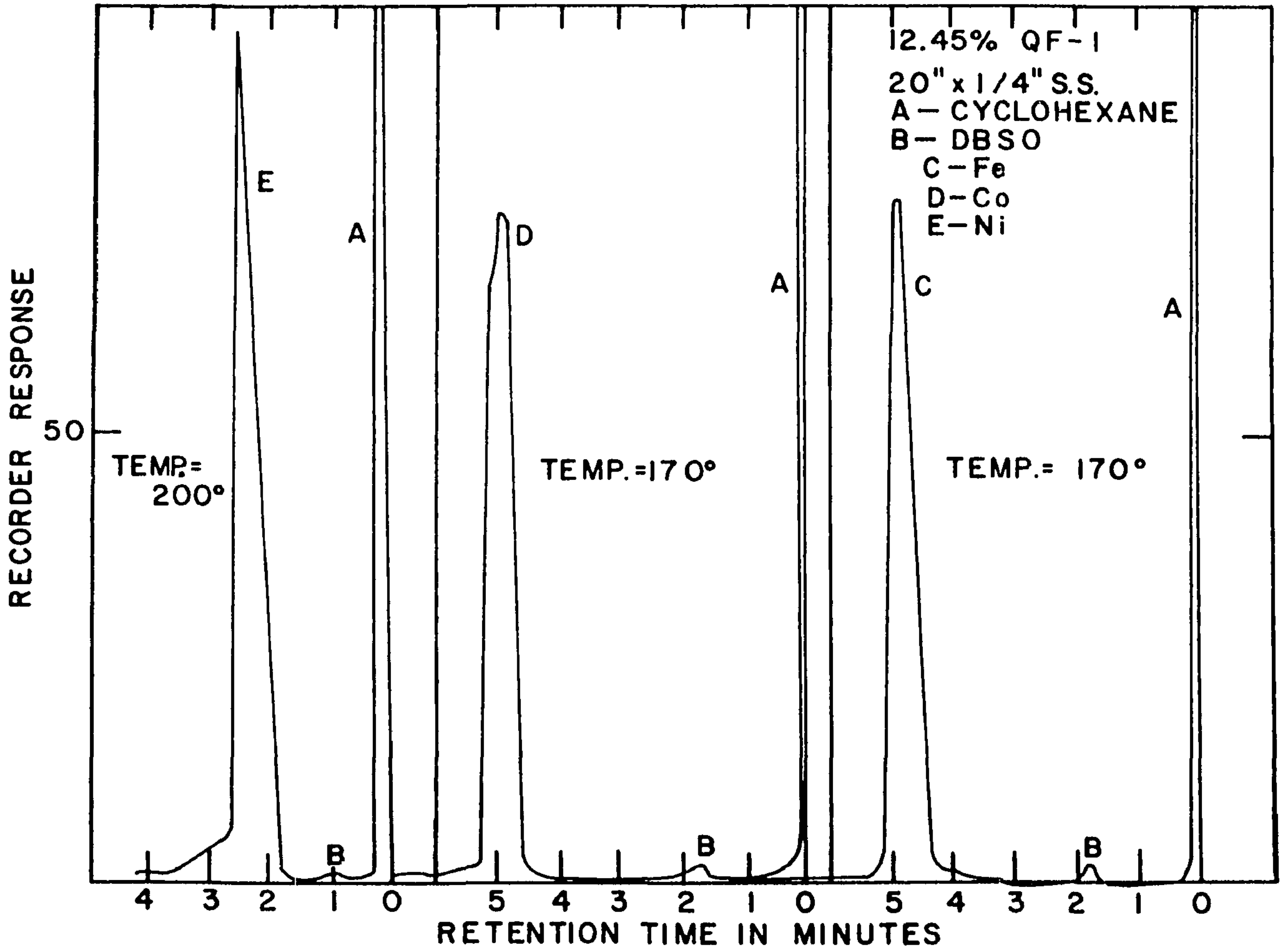


Figure 4. 9. Gas chromatograms of iron, cobalt and nickel as H(FHD)-DBSO mixed-ligand complexes

used additional contributions to the retention volume from liquid surface adsorption, complexation in the bulk liquid and/ or association in highly oriented liquid phase layers cannot be ignored.

Evidence has been presented which indicates column loading is a sum of solid support adsorption and association or complexation in the liquid phase. All other interactions are liquid phase dependent. These non-ideal phenomena are observed to a lesser extent when Dexsil 300 GC is used as a liquid phase. For this reason Dexsil 300 GC should be used for studies with mixed-ligand systems. The value of preparing inert complexes cannot be minimized. By elimination of possible coordination sites, specifically be the use of mixed-ligand complexes, non-equilibrium interaction is diminished.

V. AN INVESTIGATION OF THE ELECTRON CAPTURE DETECTOR FOR THE DETERMINATION OF MIXED-LIGAND COMPLEXES

A. Introduction

This work will describe a study of the electron capture detector in regard to its usefulness as a detector for the determination of mixed-ligand lanthanide complexes. Several parameters such as flow rate of purge gas and pulse interval were investigated and data are presented which illustrate the utility of this detector.

The electron capture detector has seen recent widespread application in the determination of metal chelates (8, 22, 44, 55, 59, 60, 115, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 140, 175, 182, 190, 191). The inherent sensitivity to perfluorinated molecules has allowed detection limits as low as 10^{-13}g metal (132). As described in Section III, the flame ionization detector has been used in the development of the reported method for the determination of the lanthanides. The detection limit reported was 2 x 10^{-7}g metal. In an effort to extend this method to lower concentrations the electron capture detector was investigated.

B. Experimental

1. Apparatus

a. Gas chromatograph A Hewlett-Packard Model 5756B gas chromatograph equipped with a ^{63}Ni electron capture detector and a hydrogen flame ionization detector was used for all studies. The chromatograms were recorded with a Hewlett-Packard model 7128A strip chart recorder.

2. Mixed-ligand complexes

The mixed-ligand complexes of the lanthanides with H(FHD) and

DBSO were prepared by the solvent extraction procedure outlined in Section III.

C. Results and Discussion

Considerable effort was expended in establishing optimum operating conditions for the particular electron capture detector accompanying the Hewlett-Packard instrument. The maximum sensitivity was achieved when the detector was operated in the pulse mode using a pulse of 150 μseconds. This interval allowed the detection of 10^{-12}g dichlorobenzene. After suitable operating conditions were established various attempts at the successful elution of lanthanide complexes were made. No detector response was found until samples approximately 0.01 M in complex were injected. These samples are within the range of detection by the flame ionization detector. When the chelates were eluted at this concentration, the electron capture detector immediately became overloaded. The resultant chromatogram showed a broad plateaued peak which required 45 minutes before original base line was regained. The electron capture detector did have high sensitivity to the mixed-ligand complexes; however, the irreversible adsorption of low level concentrations of the chelates on the column prevented elution of samples in the concentration ranges low enough to avoid detector overload. To determine precisely how sensitive the detector was for the complexes, a 100 to 1 split was attached to the exit end of the column, immediately preceding the detector inlet. Samples of approximately 0.01 M chelate were injected into the column. Even after a split of 100 to 1 the EC detector showed evidence of overload. By increasing the flow rate of the argon-methane purge gas, the detector residence time of the species to be determined can be shortened. This has the effect of diluting the concentration of the species in the detector during pulse intervals. The flow of the argon-methane purge gas was systematically increased from 50 ml/min to 444 ml/ min. As the flow increased, the peak shape improved markedly. At a flow of 444 ml/ min., a peak of reasonable shape was obtained for all of the lanthanide chelates. This peak was still broad, requiring approximately eight miutes before return to the original base line. The improvement in peak shape shows the detector to be extremely sensitive for the complexes; at flow rates of 444 ml/ min and a 100 to 1 split, approximately 10^{-11}g lanthanide are being detected.

Although of no practical utility at this time, when column technology arrives at a point where column adsorption is eliminated, the mixed-ligand complexes of the lanthanides will be easily detected by the electron capture detector at the ultra trace level.

VI. AN INVESTIGATION INTO THE UTILITY OF LANTHANIDE-FHD CHELATES AS PARAMAGNETIC SHIFT REAGENTS FOR NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A. Introduction

This work will describe the development of a series of new paramagnetic shift reagents for use in nuclear magnetic resonance spectroscopy, nmr. Data are presented which illustrate the improved chemical shifts of interior substrate protons when lanthanide complexes of FHD are used a shift reagents. Various substrates were studied and chemical shifts are reported for several substrate types.

B. Experimental

1. Apparatus

a. Spectrometer All spectra were recorded on a Varian A60 nmr Spectrometer. In every case, CCl_4 was the solvent and TMS (τ 10.00) was the internal standard.

2. Reagents and materials

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

b. Substrates All substrates were reagent grade and used without purification.

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

The ligand H(FHD) was synthesized by the procedure described in Section III.

3. Techniques

a. Synthesis of shift reagents To prepare the lanthanide shift reagents, 5.0 g of the appropriate rare earth oxide was dissolved in concentrated nitric acid and evaporated to dryness yielding the rare earth nitrate hexahydrate. 10.12 g of H(FHD) was dissolved in approximately 5 ml of absolute methanol and 8.01 ml of 4.12 N sodium hydroxide was added to the methanolic solution. 4.9 g (0.011 Moles) of rare earth nitrate was dissolved in a minimum amount of methanol, the pH was adjusted to 4-6 (pH paper) using 4.12 N sodium hydroxide. The two solutions were combined and formed a homogeneous mixture. The mixture was then added to 100 ml of water dropwise over a one-half hour period with rapid stirring. The complex formed a yellow oil which was separated from the aqueous layer. The oil was then dissolved in methylene chloride and recrystalized, the resultant solid was fragile and was dried in vacuo for 24 hours. The final yield was 92 %.

C. Results and Discussion

Rondeau and Sievers (126) have shown that lanthanide complexes containing fluorinated side chains produce greater chemical shifts and are more soluble than the analogous hydrocarbon compounds. The shift reagents of Sievers are not fully fluorinated, possessing a t-butyl proton group on each ligand. These t-butyl groups contribute 27 protons which can interfere with spectral interpretation of the desired substrate.

The chelates of H(FHD) are fully fluorinated and void of the t-butyl group. Chelates were prepared from all of the lanthanide oxides by the procedure given above. Microanalysis was performed on $Eu(FHD)_3$, as a representative complex. Results for this analysis are presented in Table 6.1.

Table 6.1. Analysis of the $Eu(FHD)_3$ shift reagent

Compound	% Metal Calcd.	% Metal Found	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found
$Eu(FHD)_3$	14.16	14.22	23.51	24.29	0.28	0.40

Upon drying in vacuum over P_4O_{10} for only two hours, the complexes were found to exist as the monohydrate, as indicated by Karl Fischer titration. No special precautions were taken to insure the anhydrous condition of the complexes during use as shift reagents. Apparently the presence of water has little or no effect on the shift capacity of the reagent.

The complexes of the lanthanides were found to be quite soluble in CCl_4, dissolving to the extent of 300 mg/ml. When polar substrates were present the solubility of the complexes was even higher. This behavior is similar to that reported by Rondeau and Sievers (126).

The shift capacity of the H(FHD) complexes of each of the lanthanides was determined. For all studies di-n-butyl ether was used as the substrate. The complexes with lanthanum, lutetium and gadolinium induced no paramagnetic shift; complexes of praseodymium, neodymium, samarium, dysprosium and holmium gave shifts to higher field; complexes of erbium, europium and ytterbium induced shifts to lower field. These shifts are in agreement with those reported for other shift reagents of these lanthanides (22, 34, 5).

Except for studies with $Eu(FHD)_3$ line broadening was extensive. Only for $Dy(FHD)_3$ and $Yb(FHD)_3$ could fine structure still be seen and then only in the methyl resonances. With the exception of samarium and neodymium shifts were greater than those observed with the europium complex. The erbium and holmium complexes produced the shifts of greatest magnitude.

The utility of the europium complex as a shift reagent was determined for various substrates, including di-n-butyl ether, di-n-butyl ketone, n butyl amine, tri-n- butyl amine, di-n-butylsulfoxide and tri-n-butylphosphate. Significant shifts were observed for all five of the substrates. The shifts for DBSO and TBP were less than with other substrates. Both of these substrates are known to form isolable complexes with europium. If these mixed-ligand complexes are formed, the exchange between complexed and free substrate would be lower, giving rise to smaller observed shifts. Examples of the unshifted spectrum of di-n-butyl ketone and the shifted spectrum obtained at a ratio of europium complex to substrate of one, are shown in Figure 6.1 and Figure 6.2. No spectral interference is found from protons on the europium complex. Each resonance is sharp with excellent fine structure. The intense resonance at 1.3 ppm results from the three protons remaining on the H(FHD) molecules after complexation. This resonance offers no interference to spectral interpretation and can be used as a rough indication of when the maximum shift is reached. The resonance can be seen to shift upfield, from 9.5 ppm with low shift reagent to substrate ratio, to 1.3 ppm at a shift reagent to substrate ratio of one.

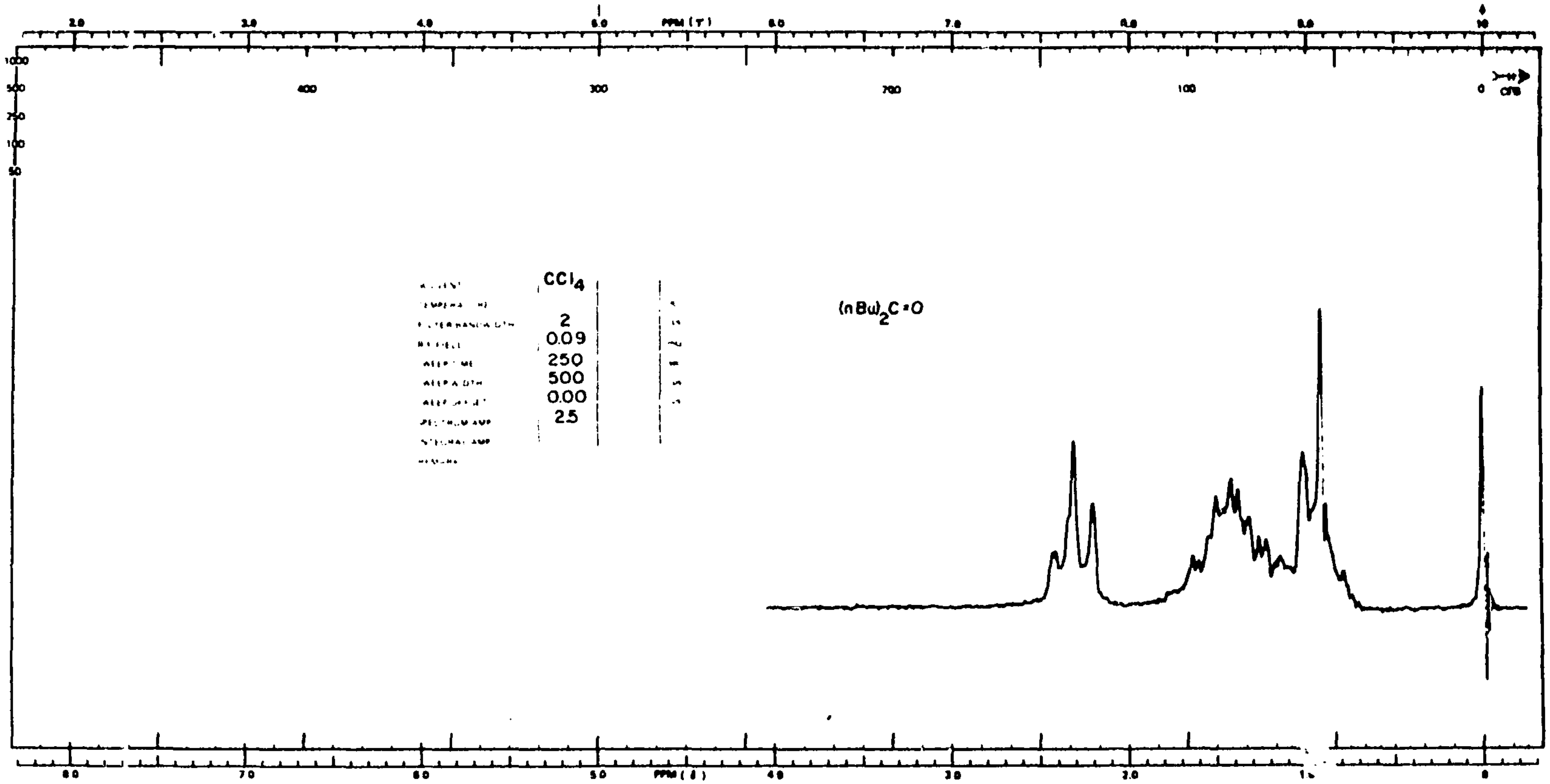


Figure 6.1. ^{1}H nmr spectrum of di-n-butyl ketone

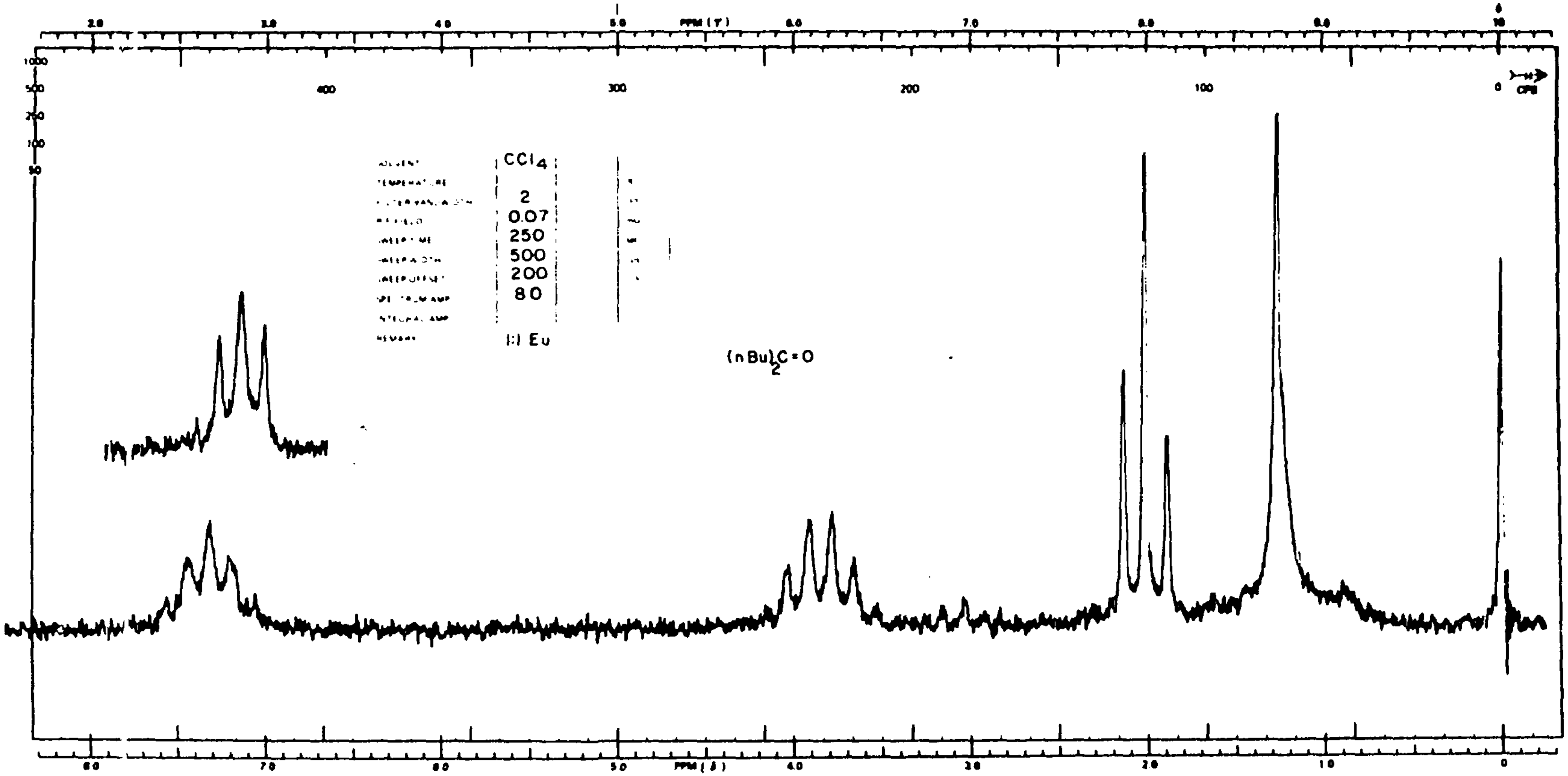


Figure 6.2. ^{1}H nmr spectrum of di-n-butyl ketone after addition of Eu(FHD)$_3$ to a 1:1 ratio

The shifts observed for the protons several carbon atoms removed from the electronegative center of the substrate are greater than those reported by other workers (126, 138) for other europium shift reagents. This increased shift for the remote protons in probably a result of the complete fluorination and the absence of steric hinderence from the t-butyl group present in the other shift reagents. Both of these effects would allow closer approach of the substrate to the paramagnetic center, thereby causing the more remote protons to experience more of the paramagnetic field of the lanthanide. This increased exposure to the paramagnetic center would result in the larger induced shifts observed.

In summary, the lanthanide complexes of H(FHD) are excellent shift reagents. Their solubility is extremely high and because of total fluorination and the lack of bulky ligand substituents the shifts induced are greater for remote protons than those of the prior art.

VII. SUMMARY

The mixed-ligand complexes of the lanthanides with H(FHD) and DBSO can be quantitatively separated and determined by gas chromatography. Separations can be achieved for mixtures containing the lanthanides on an every-other-one basis. using short columns containing 6.46 % Dexsil 300 GC on Chromosorb W-HP and the technique of temperature programming. Flame ionization detector detection limits were found to be 0.2 µg metal for all of the lanthanides.

The partitioning of the mixed-ligand complexes was found to be a function of bulk liquid partitioning, adsorption on the liquid surface, adsorption on the solid surface and association within the bulk liquid and/or at the interficial boundaries.

The non-equilibrium column phenomena observed are a function of the percentage of liquid phase present as well as the type of liquid phase used. Columns prepared with Dexsil 300 GC perform satisfactorily for the determination of mixed-ligand complexes, but even these columns possess non-equilibrium properties which prevent the detection of ultra trace quantities of complexes.

The electron capture detector is extremely sensitive to the mixed-ligand complexes of the lanthanides. It is presently useless as a detector for the determination of the lanthanides because of severe column adsorption of low level chelate concentrations. The amounts of chelates that will be eluted from the column are too high for the capacity of the detector and severely overload it.

The lanthanide complexes of H(FHD) are extremely good paramagnetic shift reagents for nuclear magnetic resonance spectroscopy. In particular, the europium complex allow excellent shifts without line broadening. The shifts realized for protons on carbon atoms several atoms removed from the basic functional group of the substrate are greater than those induced by other shift reagents.

VIII. SUGGESTIONS FOR FUTURE WORK

The technique of synergistic solvent extraction should be applicable to other chemical systems. By judicious selection of β-diketone. many mixed-ligand complexes of high thermal stability should be readily formed. The most fruitful areas of investigation should be the latter row transition metals and the alkaline earths. The research described in this thesis should lay the ground work for the preparation of chelates of high thermal stability for those metals known to form diketonates of unstable thermal properties, such as manganese, zinc, cadmium, lead and the alkaline earths.

Detailed efforts into the synthesis of new liquid phases and solid supports of high thermal stability, yet void of column loading phenomena should prove productive. With the advent of new phases and supports allowing quantitative elution of metal chelates, several methods for ultra trace metals should be rapidly developed.

The synthesis of new ligands such as the tetradentate and thioketones should add a new dimension of selectivity to inorganic gas chromatography. By proper selection of ligands, synthesized to possess the optimum in complex formation constants, several new volatile complexes should be easily prepared.

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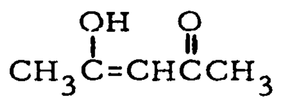
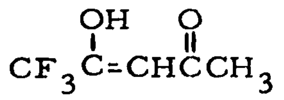
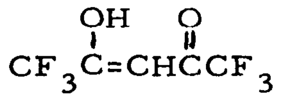
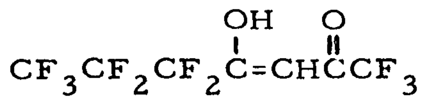
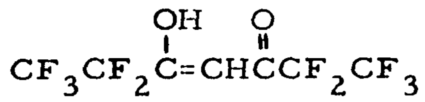
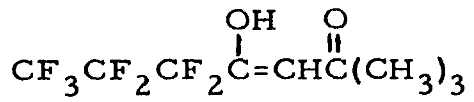
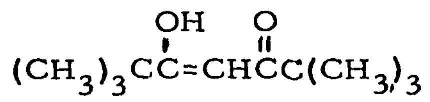
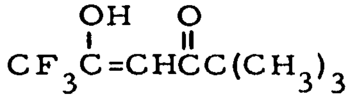
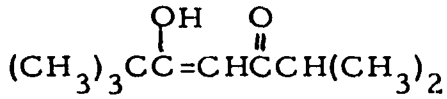
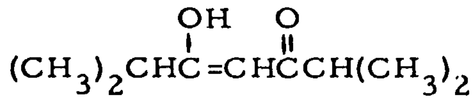
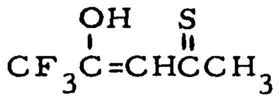
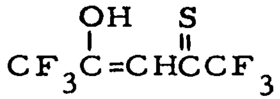
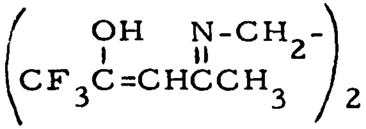
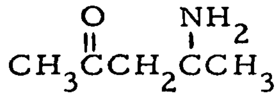
X. APPENDIX

Stucture and nomenclature

Name	Abbreviation	Structure
2,4-pentanedione	H(ACAC)	 $\mathrm{CH_3\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}CH_3}$
1,1,1-trifluoro-2,4-pentanedione	H(TFA)	 $\mathrm{CF_3\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}CH_3}$
1,1,1,5,5,5-hexafluoro-2,4-pentanedione	H(HFA)	 $\mathrm{CF_3\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}CF_3}$
1,1,1,2,2,3,3,7,7,7-decafluoro-4,6-heptanedione	H(DFHD)	 $\mathrm{CF_3CF_2CF_2\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}CF_3}$
1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione	H(FHD)	 $\mathrm{CF_3CF_2\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}CF_2CF_3}$
1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6,-octanedione	H(FOD)	 $\mathrm{CF_3CF_2CF_2\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}(CH_3)_3}$
2,2,6,6-tetramethyl-3,5-heptanedione	H(THD)	 $\mathrm{(CH_3)_3C\overset{OH}{\overset{\vert}{C}}=CH\overset{O}{\overset{\Vert}{C}}C(CH_3)_3}$

Name	Abbreviation	Structure
1,1,1-trifluoro-6,6-dimethyl-2,4-heptanedione	H(PTA)	 $CF_3\overset{\overset{OH}{\mid}}{C}{=}CH\overset{\overset{O}{\Vert}}{C}C(CH_3)_3$
2,2,6-trimethyl-3,5-heptanedione	IBPM	 $(CH_3)_3C\overset{\overset{OH}{\mid}}{C}{=}CH\overset{\overset{O}{\Vert}}{C}CH(CH_3)_2$
2,6-dimethyl-3,5-heptanedione	H(DMH)	 $(CH_3)_2CH\overset{\overset{OH}{\mid}}{C}{=}CH\overset{\overset{O}{\Vert}}{C}CH(CH_3)_2$
1,1,1-trifluoro-2-hydroxylpent-2-en-4-thione	H(T-TFA) or HFAS	 $CF_3\overset{\overset{OH}{\mid}}{C}{=}CH\overset{\overset{S}{\Vert}}{C}CH_3$
1,1,1,5,5,5-hexafluoro-2-hydroxylpent-2-en-4-thione	H(T-HFA)	 $CF_3\overset{\overset{OH}{\mid}}{C}{=}CH\overset{\overset{S}{\Vert}}{C}CF_3$
bis-trifluoroacetylacetone-ethylenedi-imine	$H_2(enTFA_2)$	 $\left(CF_3\overset{\overset{OH}{\mid}}{C}{=}CH\overset{\overset{N-CH_2-}{\Vert}}{C}CH_3\right)_2$
4-aminopent-3-en-2-one	AMO	 $CH_3\overset{\overset{O}{\Vert}}{C}CH_2\overset{\overset{NH_2}{\mid}}{C}CH_3$

Name	Abbreviation	Sructure
Tri-*n*-butylphosphate	TBP	$(C_4H_9O)_3\text{-P}\rightarrow\text{O}$
Di-*n*-butylsulfoxide	DBSO	$(C_4H_9)_2\text{-S}\rightarrow\text{O}$

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