1968

Gas chromatography of some metal chelates of benzoyltrifluoroacetone and thenoyltrifluoroacetone and of the complexes of the rare earths with the mixed ligands hexafluoroacetylacetone and tri-n-butylphosphate

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by

William Cunningham Butts

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INTRODUCTION

The determination of metals by gas chromatography (G.C.) is a new technique that is being rapidly developed. Gas chromatography offers the advantages of combined separation and determination processes, as well as the capability to analyze for major or trace constituents. The variety of detection systems available provides a broad range of selectivity and sensitivity.

The inherent disadvantage of G.C., however, is the necessity that a sample be volatile at the operating temperature of the instrument; sufficient volatility for gas chromatography is a vapor pressure of approximately ten millimeters of mercury. Because gas chromatographs are not conveniently operated at temperatures in excess of 300°C, there is a severe limitation on the types of inorganic compounds that can be chromatographed.

Early work with inorganic gas chromatography involved the use of volatile metal halides. Such compounds, however, are frequently difficult to prepare and handle.

In 1955 Lederer (44) first suggested gas chromatographing metal chelates of the β-diketone acetylacetone. It was not until 1959, however, that Duswalt (23) actually chromatographed several acetylacetonates. In 1963, Sievers et al. (79) published a paper describing the gas chromatography of several metal chelates of acetylacetone (HACAC)[1], trifluoroacetylacetone (HTFA), and hexafluoroacetylacetone (HHFA). The most important aspect of this paper was that it demonstrated the remarkable increase in the volatility of the chelates with the fluorinated ligands. Table 1 gives the boiling points of these three β-diketones. It can be seen that the volatility of the ligands is a function of the degree of fluorination rather than of the molecular weight. A reduction in van der Waals forces and a decrease in intermolecular hydrogen bonding have been offered as possible reasons for the increased volatility of the fluorine-containing chelates.

Table 1. Properties of several β-diketones

Ligand	Molecular weight	Boiling point	pK_{HA}	Log P^a	Reference
HACAC	100	137	9.0	0.8	66
HTFA	154	104	6.6	0.1	66
HHFA	208	66	4.6		3
HBTA	216		6.3	2.1	82
HTTA	222		6.2	1.6	66

[a] Benzene used as organic phase.

Since 1963, gas chromatography of metal chelates has become an active research area as evidenced by the rapidly increasing number of publications, several of which are

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[1] See APPENDIX A for structures and nomenclature of ligands.

discussed in the following LITERATURE REVIEW. The majority of these studies were performed with the chelates of HTFA, probably because of the relative ease of formation of the HTFA chelates as compared to those of HHFA.

The formation of the chelates is another important consideration in the development of an analytical technique utilizing gas chromatography of metal chelates. It is necessary that the chelate be formed quantitatively, and it is desirable that it be formed rapidly, with a minimum of manipulation, and in an organic solvent to facilitate introduction into the chromatograph. Solvent extraction can meet all of these criteria. β-diketones have been extensively used in solvent extraction and the extraction properties of many of them have been characterized. Table 1 contains the dissociation constants (K_{HA}) and partition coefficients (P) for several β-diketones that have been studied as solvent extractants. Although the values of log P for the ligands are given in the table, these are directly related to the distribution ratios for the chelates of the corresponding ligand (82, p. 32). A low value of pK_{HA}, permitting extraction from more acidic solutions, and a high value of log P are desirable.

Of the ligands cited in Table 1, thenoyltrifluoroacetone (HTTA) has been the most comprehensively studied as an extractant. As can be seen from the pK_{HA} and log P values in the table, it and benzoyltrifluoroacetone (HBTA) possess the most favorable extraction properties of the β-diketones. For this reason, it was decided to study the application of gas chromatography to the chelates of HTTA and HBTA. Benzoyltrifluoroacetone was of particular interest, because its chelates had been found to be generally more volatile than those of HTTA.

The potential of gas chromatography to separate and analyze very similar compounds makes the application of G.C. to the analysis of rare earths of prime interest. The chelates formed between the rare earths and HPIV[1] or HFOD have been successfully chromatographed and some separations have been achieved. Neither ligand, however, holds much promise of being a good extractant for the rare earths.

As indicated earlier, hexafluoroacetylacetone forms extremely volatile chelates, in fact, the most volatile chelates yet found. Hexafluoroacetylacetone, however, is a very poor extractant. It reacts with water to form a dihydrate involving the carbonyl groups which hinders its complexation with the metal ion. Both the ligand and its chelates also have very low distribution ratios.

Many of the β-diketones, including HHFA, have been shown to form mixed-ligand complexes which exhibit synergically enhanced extraction. Synergism is defined as the cooperative effect of separate agents such that the total effect is greater

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[1] See APPENDIX A for structures and nomenclature of ligands.

than the sum of the individual effects. Synergism has been most extensively studied for mixed-ligand systems employing a β-diketone and an organophosphorus compound. Tri-n-butylphosphate (TBP) is one of the organophosphorus compounds successfully used in synergic extractions with the β-diketones. TBP has an advantage in a G.C. study in that its molecular weight is lower than that of most other organophosphorus compounds. This would indicate its mixed complexes should be more volatile.

For the reasons set forth above, it was decided to study the mixed-ligand system HHFA and TBP as a gas chromatographic reagent for the rare earths. A G.C. reagent is a system that reacts quantitatively with a species that cannot be gas chromatographed forming a new species that can be analytically chromatographed.

Both the study of the application of G.C. to the chelates of HBTA and HTTA and the investigation of the mixed ligands HHFA and TBP as a G.C. reagent for the rare earths were undertaken with a view toward analytical applications. It was not the intent of this thesis research to establish an operable technique, but rather to assess the possibilities of developing the previously mentioned studies into such a technique.

LITERATURE REVIEW

The work reported in this thesis is concerned with the application of gas chromatography to the metal chelates of HTTA and HBTA and to the complexes of the rare earths with the mixed ligands HHFA and TBP. Therefore, this review will principally cover the gas chromatography of metal chelates of the β-diketones. Brief coverage will also be given to mixed-ligand complexes as they pertain to the HHFA and TBP system.

An excellent monograph on the gas chromatography of metal chelates by Moshier and Sievers (53) has been published. The reader is referred to this book for a complete review of the literature prior to 1965.

Attempts to chromatograph inorganic compounds other than chelates have met with varying success. The most notable of these is the work by Juvet and Fisher (38). They have prepared, by means of an an in-line reactor, and chromatographed the fluorides of 13 elements. Quantitative results are given for U, Se, S, Te, W, Mo, and Re. Several other applications of G.C. to inorganic halides are reviewed by Keller (40).

Lederer (44) first mentioned the application of G.C. to metal chelates in 1955, when he suggested the separation of the rare earths by gas chromatography of their chelates with acetylacetone. Duswalt (23), in 1959, reported successfully gas chromatographing the acetyacetonates of Be, Zn, and Sc. At about the same time, Biermann and Gesser (11) reported the gas chromatographic elution of the Be, Al, and Cr chelates of HACAC. Little more appeared in the literature until 1963, when Sievers _et al_. (79) published a paper on the gas chromatography of several chelates of HHFA, HTFA, and HACAC. This paper demonstrated the remarkable increase in the volatility of chelates of fluorinated β-diketones as compared to those of acetylacetone and proposed that the increase in volatility may be due to a reduction in van der Waals forces and possibly to a decrease in intermolecular hydrogen bonding. The separation of the geometrical isomers of $Cr(TFA)_3$ was also accomplished.

Since 1963 gas chromatography has become an active research field, with Sievers and his coworkers (24,25,51,53,62, 77,78,79,76,81) being the principal contributors. The range of chelates of the β-diketones that have been gas chromatographed is indicated in the selected list of references in Table 2.

Few of the publications to date, however, have been concerned with quantitative applications of the gas chromatography of the metal chelates. Hill and Gesser (35) studied the response of a flame ionization detector to chelates of HACAC, HTFA, and HHFA and concluded that increasing fluorination decreases sensitivity. They also chromatographed a series of Be, Al, and Cr chelates of trifluoroacetylacetone and noted that the analytical curves (detector response versus concentration) did not pass through the origin; this deviation they

Table 2. Selected references illustrating the scope of the gas chromatography of metal chelates of β-diketones

Metals	Ligand	Reference
Be, Al, Cr	HACAC	11
Be, Zn, Sc	HACAC	23
Be, Al, Cu, Cr, V	HACAC	76
Rh, Al, Cr	HTFA	62
Al, Ga, In, Be, Tl	HTFA	65
Co, Ru	HTFA	88
Be, Al, In, Cu, Fe, Rh, Zr, Hf	HTFA	76
Cr, Fe, Rh	HHFA	37
Ni, Co	HHFA	60
Cr, Al	HHFA	61
Co, Ru	HHFA	88
Al	HTTA	48
rare earths, Sc, Y	HPIV	24
rare earths, Sc, Y	HFOD	81
Ni, Fe, Pd, Cr, Cu, Al, Y, Be	HFOD	77

attributed to the formation of metal oxide particles in the flame. Ross and coworkers (61,62,63) performed several studies of some chelates of HACAC, HTFA, and HHFA using an electron capture detector. Greater sensitivity with increasing fluorination was noted. The lower detection limits thus found for the Cr chelates of HACAC, HTFA, and HHFA were 8.8×10^{-8}, 9.0×10^{-11}, and 3.3×10^{-11}g, respectively. The analytical curve for synthetic samples of $Cr(HFA)_3$ was regular but nonlinear over the range of 10^{-8} to 10^{-3} g/ml. A comparison of the response of flame ionization and electron capture detectors to metal chelates by Albert (1) confirmed the results of Hill and Gesser, and Ross. Schwarberg *et al.* (65) quantitatively analyzed synthetic mixtures of the chelates of Be, Al, Ga, and In with HTFA with a relative mean error of 2% using a thermal conductivity detector. Synthetic solutions of $Al(TTA)_3$ were also gas chromatographically analyzed with a thermal conductivity detector by Michino et al. (48).

None of these studies, however, involved sampling under practical conditions. In all cases the pure solid chelates were prepared and then dissolved in an organic solvent. Some authors (63,65) did recommend that solvent extraction be studied as a sampling technique. Morie and Sweet (50) were the first to extract and then quantitatively chromatograph metal chelates. By extraction with HTFA in benzene they determined Al and Ga with 2.3% relative mean error and In with a relative mean error of 5.2% over the concentration range of 10^{-3} to 10^{-2} molar. Scribner et al. (69) previously reported extracting Cu, Fe, and Al with HTFA in chloroform, but gave no quantitative G.C. data. Using the same system, Moshier and Schwarberg (52) analyzed an alloy for Fe, Cu, and Al with better than 2% relative mean error. Stokely (84) has studied combined extraction and gas chromatography with HTFA and HHFA. Although good results were obtained with HTFA, HHFA did not yield quantitative extractions and could not be used for quantitative analysis.

Sievers, Connolly, and Ross (77) have developed a technique using HFOD that employs direct reaction of the ligand with the solid sample. Although the method gave quantitative results, it has the disadvantages of requiring a finely powdered sample, encapsulation in a small glass tube, and reaction times of two hours or longer at elevated temperatures, and it appears to be of uncertain utility with minor constituents.

The most recent development in metal chelate G.C. has been the successful chromatography of chelates of the rare earths. Sievers and coworkers (24,81) have gas chromatographed the chelates of the rare earths with the β-diketones HPIV and HFOD. In both cases solid chelates were prepared, then dissolved in an organic solvent, and chromatographed. Each series of chelates showed a regular increase in retention time with increasing ionic radius of the corresponding trivalent rare earth ion. Because of the lanthanide contraction this is in the opposite order of increasing mass and was attributed to decreased dipoles in the chelates of the smaller ions (81).

Scribner and Kotecki (68) reported the solvent extraction of several divalent metals with the mixed ligands HTFA and isobutylamine in chloroform; they also mentioned that several of these mixed-ligand complexes were successfully gas chromatographed. The discovery that mixed-ligand complexes can be gas chromatographed presents yet another area of inorganic gas chromatography to be explored.

Although β-diketones such as acetylacetone (83) and thenoyltrifluoroacetone (56) have been extensively used as solvent extractants, they have been found to have limited use in the extraction of metal ions having coordination numbers greater than the charge on the ion. In such cases, hydrates are formed which have low distribution ratios. HHFA forms nonhydrated chelates having low distribution ratios (67,84) and also forms hydrated chelates having even lower distribution ratios.

Because of the great volatility of its chelates (10,19, 78), HHFA is subject to consideration for G.C. studies despite its ineffectiveness as an extractant. Synergic extraction using HHFA as part of a mixed-ligand system offers the best possibility of improving the extraction of the complexes of HHFA. Synergic extraction of copper and zinc using HHFA and a neutral adduct have been reported (17,18,45,89). Apparently the formation of a dihydrate by the ligand HHFA (3,64) does not greatly obstruct complexation in these systems. The question remains whether the mixed complexes are thermally stable and volatile. Bertrand and Kaplan (10) have sublimed $Cu(HFA)_2 \cdot 2H_2O$ without dehydration. Reynolds (60) has reported gas chromatographing the complexes of nickel and cobalt(II) with the mixed ligands HHFA and dimethylformamide.

Of the classes of organophosphorus compounds used in mixed-ligand extractions, the phosphates have the greatest volatility (14), because they are the least polar. They have also been found to elute most rapidly from a G.C. column (9). A similar trend is expected for the complexes.

The most widely used organophosphate in synergic extraction is tri-n-butylphosphate. It has been used in mixed-ligand systems with HTTA for the extraction of uranium (as uranyl) (2), thorium (33), rare earths (21,33,72), and transition metals (36,70). It has also been used with HBTA (2,57) and HACAC (2). Healy (34) has reported the synergic effect to be greatest if cyclohexane is used as the diluent. The complete development and literature of synergism is thoroughly discussed by Carey (15).

Some related work that should be mentioned in this review is that by Berg and coworkers (5,6,7,8) who have studied the vapor pressure-temperature dependence and fractional sublimation separation of a great many chelates of the β-diketones. The vapor pressure data was very useful in preliminary G.C. studies, and the fractional sublimation appears to possess some utility as an analytical technique, particularly for the chelates of acetylacetone. Eisentraut and Sievers (25) have performed a comprehensive thermogravimetric study of the chelates of the β-diketones, and this study is a useful source of data for preliminary gas chromatographic studies.

APPARATUS AND REAGENTS

Gas chromatographic studies were performed on a Beckman GC-4 gas chromatograph equipped with an on-column inlet, prevaporization inlet, thermal conductivity detector, and dual hydrogen flame detector. Sample injection employed Hamilton Microsyringes. A Bristol model 560 Dynamaster recorder with a Disc Integrator recorded the chromatograms.

Solid support and liquid partitioning agents were obtained from Applied Science Laboratories. Pyrex, borosilicate glass, tubing was used for the glass columns. Metal columns were prepared from laboratory stock copper and stainless steel tubing. Swagelock fittings were used on all columns. A Burgess Vibro-graver was used to vibrate the columns during the packing procedure. Helium from laboratory stock was used for all studies with the thermal conductivity detector, and high-purity ("Zero-gas") helium, air, and hydrogen were used with the flame ionization detector. The "Zero-gases" were supplied by the Matheson Company.

Infrared spectra were obtained with a Beckman IR-7 infrared spectrophotometer. A Cary Recording Spectrophotometer, model 14, was used for ultraviolet spectra. A Beckman, model G, pH meter with a fiber-type saturated calomel reference electrode and a glass indicator electrode was used for all pH measurements. The fluorescence spectrum of the europium complex was obtained using an Aminco-Bowman spectrophotofluorimeter with a Moseley X-Y recorder.

Solutions of the rare earths were prepared by dissolving 99.9% pure rare earth oxide (purified by ion exchange at this Laboratory) in dilute acid, evaporating to near dryness, and diluting to standard volume.

Thenoyltrifluoroacetone and benzoyltrifluoroacetone were recrystallized twice from hexane. Hexafluoroacetylacetone was redistilled at 66°C. All three β-diketones were obtained from Peninsular ChemResearch.

Tri-n-butylphosphate (Fisher Scientific), tri-n-butylphosphine oxide (Carlisle Chemical Works), cyclohexane (Matheson, Coleman, and Bell), and benzene (Baker and Adamson) were used without further purification.

All other reagents were analytical grade.

EXPERIMENTAL PROCEDURES

Analytical Procedures

Metal analysis

All metal analyses were performed by direct or indirect titrations with ethylenediaminetetraacetic acid (EDTA). Standard rare earth chloride solutions and aqueous phases from extractions involving the rare earths were analyzed by direct titration with EDTA using Xylenol Orange as the indicator (41). Scandium and yttrium were determined in the same manner as the rare earths.

The solid chelates of HBTA and HTTA were wet ashed with a mixture of nitric and perchloric acids prior to analysis for the metal content. Either a direct titration with EDTA or a back titration with a standard solution of $Cu(NO_3)_2$ using NAS (30) as the indicator was used for the actual determination.

Thermogravimetric analysis

Thermograms were run of the chelates of HBTA and HTTA in order to determine the degree of hydration. The method employed, though unsophisticated, was satisfactory for this purpose. An approximately 30-milligram sample of the chelate was accurately weighed in a small platinum boat. The boat containing the sample was then placed in an oven containing a helium atmosphere. At one hour intervals the boat was removed, weighed, and replaced in the oven at a higher temperature. A plot of weight loss versus temperature provided the necessary thermogram. Complete thermograms of the chelates could not be obtained by this method because the maximum obtainable temperature of the oven was approximately 240°C.

Gas Chromatographic Procedures

Column preparation

The method used to prepare the column packings is discussed fully by Guerin (31, p. 19). This method is a compromise of techniques described by Parcher and Urone (55) and Smith (80). Only the manipulative details will be given in the following discussion.

Figure 1 illustrates the apparatus used. The desired quantity of dry support is placed on the frit in the tube. A solution, twice the wetting volume of the support, of the stationary phase in a volatile solvent is poured into the tube and allowed to filter through the support. A slight suction may be applied to increase the flow rate if the packing is too dense to permit gravity flow of the solution. After the excess solution has been drained off, filtered air is passed up through the packing while it is heated with heat lamps. When all the solvent has been removed, the dried packing is poured into the chromatographic columns. Uniform packing of the columns is facilitated by vibrating the columns during the filling operation.

A complete listing of the columns used in this study is given in APPENDIX B.

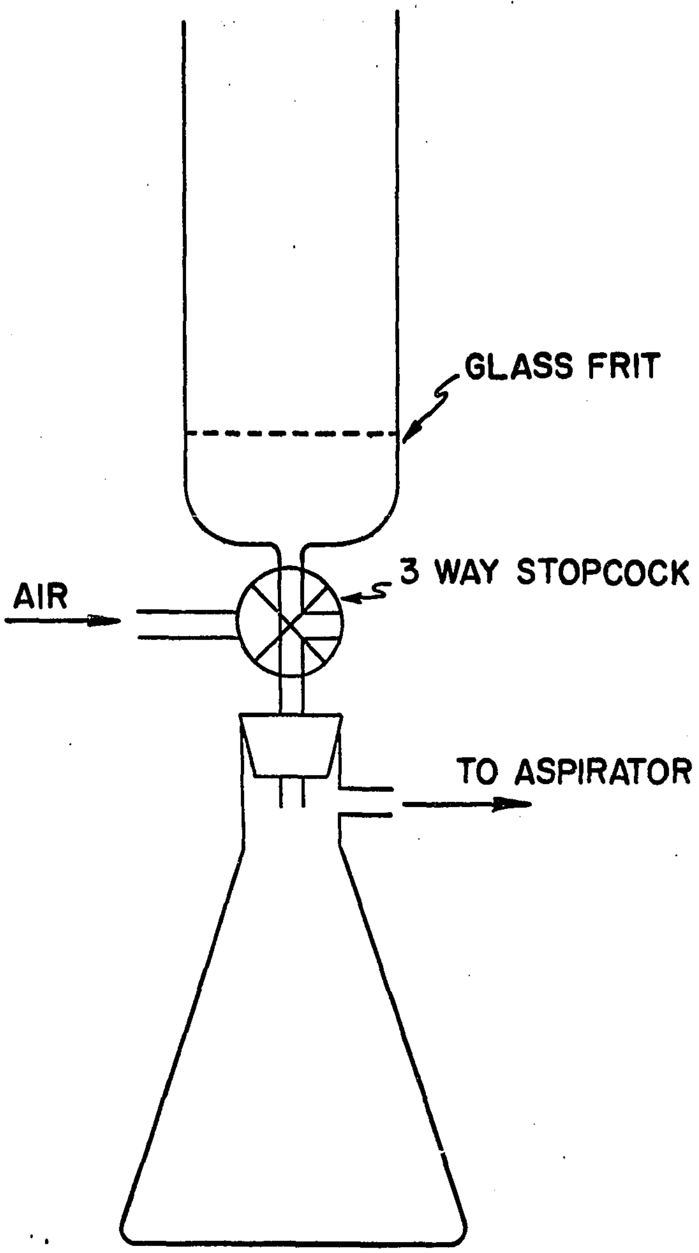

Figure 1. Apparatus used for the preparation of column packings

Sample collection

Although there are numerous devices available for the collection of the effluent from a gas chromatograph, a simple piece of glass tubing is ideal for high boiling compounds such as the metal complexes. A piece of glass tubing, four inches long with an outside diameter of three millimeters, was positioned with one end on the column exit in the detector oven and the other end extending out of the oven. The complexes readily condensed in the cooler end of the tubing and were washed out with solvents compatible with the intended additional studies of the complexes.

Operating procedure

It is desirable, particularly for quantitative work, to establish a reproducible technique for injecting the sample into the gas chromatograph. Particular care was taken to clean the syringe between injections. This was accomplished by rinsing the syringe five to ten times with pure solvent prior to sampling. Also, once the sample was injected, the syringe needle was left in the inlet for ten seconds to ensure complete vaporization.

Operating column temperatures and carrier gas flow rates were varied depending on the particular experiment being performed. These values are given throughout this thesis where they are pertinent. The inlet temperature was kept 25 to 50°C higher than the column temperature to provide complete vaporization of the sample. Larger temperature differences were avoided to minimize thermal decomposition. The detector compartment was also operated 25 to 50 degrees higher than the column oven to avoid condensation in the detector assembly.

Preparation of β-diketone Chelates

The preparation of the chelates of HBTA and HTTA has been well reported (7,59). A five per cent by weight solution of the metal nitrate was buffered immediately before use with five grams of sodium acetate for every 100 milliliters of solution. The buffered solution of the metal ion was then shaken with an alcoholic solution of excess ligand. After precipitation, which took from a few seconds to several hours depending on the metal ion, the precipitate was washed with water and collected by filtration. Heating of the solution was necessary to bring about chelation with some metals, notably chromium(III). Recrystallization was accomplished from ethanol-water or petroleum ether (7).

Extraction Procedure for Mixed-Ligand Complexes

The technique employed for the extraction of the complexes of the rare earths with the mixed ligands HHFA and TBP was very similar to that used by Carey (15) for the extraction of europium with HTTA and various phosphine oxides. It is well suited to G.C. studies because of the small volumes used and the accessibility of the organic phase.

Five milliliters of cyclohexane containing the HHFA and TBP and five milliliters of an aqueous solution of the rare earth chloride buffered to pH 5.5 with a sodium acetate buffer were placed in a glass-stoppered 15-milliliter centrifuge tube and shaken for one hour. The tubes were then centrifuged to aid phase separation. The lighter organic phase was sampled directly with a syringe for gas chromatographic studies, and a pipet was used to sample the aqueous phase for the determination of percentage extraction.

GAS CHROMATOGRAPHIC STUDY OF SOME METAL CHELATES OF HBTA AND HTTA

Results and Discussion

Because it was a purpose of this research to study the gas chromatography of chelates that can be analytically extracted, only those metals that form such chelates were studied in any depth. Some other metals that form hydrated chelates which are poorly extracted are discussed in the section Mixed-ligand complexes.

Composition of chelates and identification of eluted species

The analysis of the composition of the solid chelates of HBTA and HTTA was a necessary part of the gas chromatographic study of the chelates of these ligands. Such determinations were required to confirm that the compounds eluted from the chromatograph were the same as those injected. The hydration data for the chelates were also useful in explaining the relative solubilities of the chelates.

Table 3 contains the results for the metal analysis, by titration with EDTA, of several chelates of HBTA and HTTA. The hydration of these and other chelates as determined from the thermograms in Figure 2 and Figure 3 are presented in Table 4. The data in Tables 3 and 4 are consistent and show that the trivalent transition metal ions form anhydrous chelates with the β-diketones. The results for the divalent ions of nickel, copper, and zinc are consistent, although they

Table 3. Metal analysis of several chelates of HBTA and HTTA

Chelate	% Metal found	% Metal calculated anhydrous	% Metal calculated $\cdot H_2O$	% Metal calculated $\cdot 2H_2O$
$Fe(BTA)_3$	8.01	7.98	7.78	7.59
$Fe(TTA)_3$	7.85	7.74	7.56	7.38
$Cu(BTA)_2$	12.87	12.87	12.41	11.99
$Cu(TTA)_2$	12.48	12.51	12.08	11.68
$Zn(BTA)_2 \cdot H_2O$	12.70	13.20	12.74	12.31
$Zn(TTA)_2 \cdot H_2O$	12.27	12.84	12.40	11.99
$Ni(BTA)_2 \cdot 2H_2O$	11.20	12.01	11.58	11.19
$Ni(TTA)_2 \cdot 2H_2O$	10.90	11.68	11.27	10.90
$Al(BTA)_3$	4.08	4.02	3.91	3.81

Table 4. Thermogravimetric determination of the hydration of several chelates of HBTA and HTTA

Chelate	% Weight loss found	% Weight loss calculated $-1\ H_2O$	% Weight loss calculated $-2\ H_2O$
$Fe(BTA)_3$	<1.0	2.5	4.9
$Al(BTA)_3$	<1.0	2.6	5.1
$Cr(BTA)_3$	<1.0	2.5	4.9
$Cr(TTA)_3$	<1.0	2.5	4.8
$Cu(BTA)_2$	<1.0	3.5	6.8
$Zn(BTA)_2 \cdot H_2O$	3.2	3.5	6.8
$Zn(TTA)_2 \cdot H_2O$	4.1	3.4	6.6
$Ni(BTA)_2 \cdot 2H_2O$	5.8	3.6	6.9
$Ni(TTA)_2 \cdot 2H_2O$	6.4	3.5	6.7

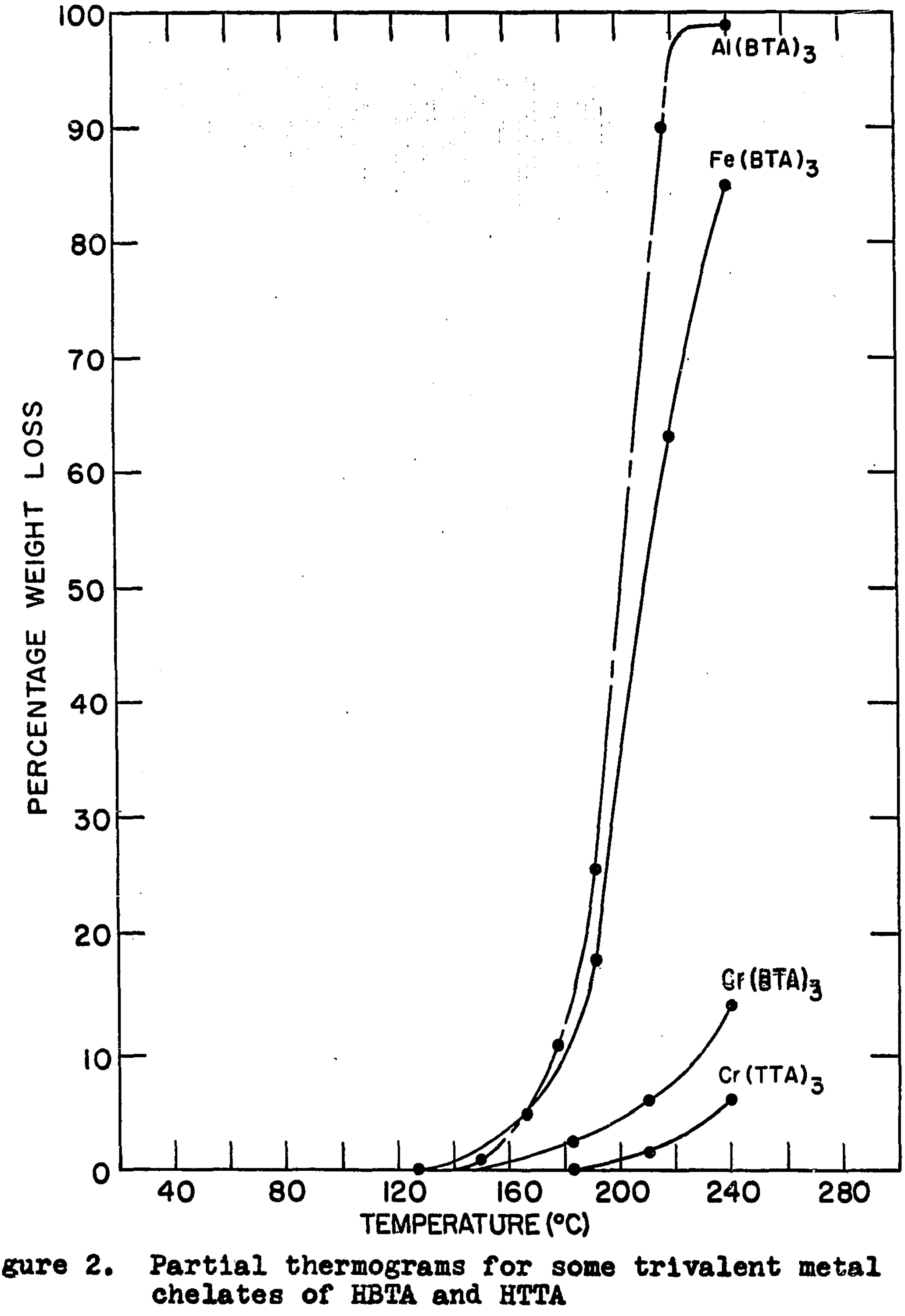

Figure 2. Partial thermograms for some trivalent metal chelates of HBTA and HTTA

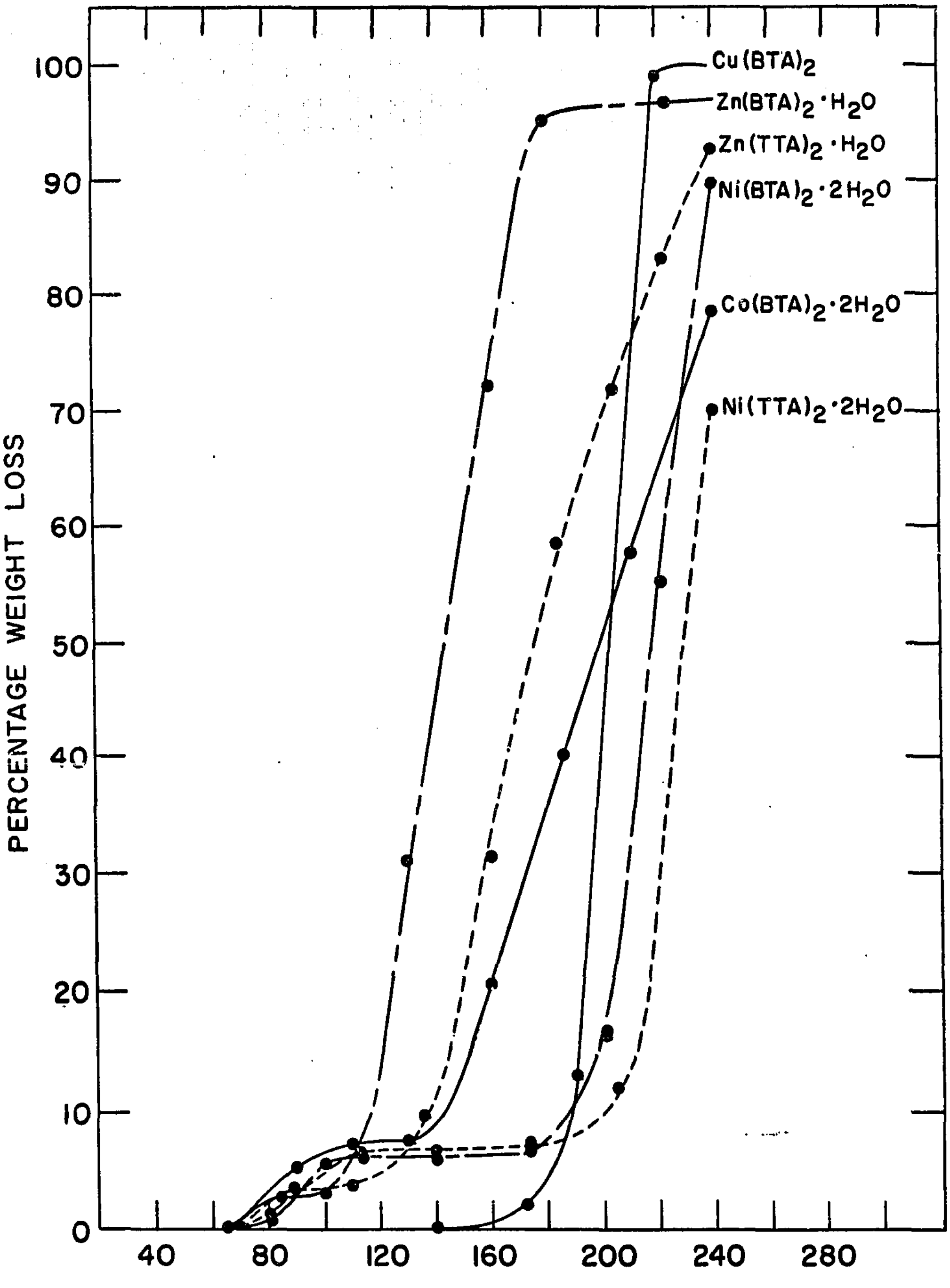

Figure 3. Partial thermograms for some divalent metal chelates of HBTA and HTTA

indicate different degrees of hydration for the chelates of the three metals. These results, however, agree with Cotton and Wilkinson (20) who report $Zn(ACAC)_2 \cdot H_2O$, $Ni(PIV)_2 \cdot 2H_2O$, and $Cu(ACAC)_2$. Rao and Li (57) report $Zn(BTA)_2 \cdot 2H_2O$; this discrepancy could be from a difference in the preparation of the chelates or from an error in analysis.

The results obtained by metal analysis and thermogravimetry were confirmed by inspection of the 3400 cm^{-1} O-H stretching frequency in the infrared spectra of the HBTA chelates of nickel, copper, and zinc. The relative intensities of this band in each spectrum are given in Table 5.

Table 5. Relative intensity of the 3400 cm^{-1} band in the infrared spectra of some chelates of HBTA

Chelate	Relative[a] band intensity (3400 cm^{-1})
$Cu(BTA)_2$	0.0
$Zn(BTA)_2 \cdot H_2O$	10.0
$Ni(BTA)_2 \cdot 2H_2O$	21.5

[a] Normalized on the 950 cm^{-1} band.

Confirmation that the eluted species were identical to the injected chelates was necessary to be certain that decomposition or other reactions did not occur in the G.C. system. Both the infrared and the ultraviolet spectra of the chelates were sufficiently characteristic for identification.

The ultraviolet spectra (Table 6) were used because much smaller effluent samples were required. The collected effluent was washed directly from the collection tube into a one-centimeter spectrophotometric cell with ethanol. The spectra of the eluted species were identical to those of the original chelates.

Gas chromatography of chelates

Although both HBTA and HTTA were selected for investigation, the greater volatility of the chelates of HBTA made it a more desirable ligand for gas chromatographic study. For this reason greater attention was given to HBTA chelates in the experiments described in the following sections. The relative volatilities of the chromium chelates of the two ligands are illustrated by the chromatograms in Figure 4. A nonpolar silicone oil, SE-30, was used as the stationary phase; therefore, the relative retention times of the chelates should reflect their relative volatilities.

These and all other HBTA and HTTA chelates were chromatographed as solutions in benzene. Benzene was selected because it is a good solvent for the chelates and would be a suitable diluent for solvent extraction with HBTA or HTTA.

The operating temperatures of the column were frequently about the same as the melting points of the chelates (175-250°C). Chelate molecules in a sample are already dispersed by being in solution, and they are further dispersed by the

Table 6. Ultraviolet spectra of several metal chelates of HTTA and HBTA in ethanol

Chelate	Wavelength (mμ)						
HTTA		264*		290		336	
$Al(TTA)_3$	228	259				343*	
$Cr(TTA)_3$			277		327		371*
$Fe(TTA)_3$		266				332*	
$Mn(TTA)_2$	228	265				341*	
$Ni(TTA)_2$		265				342*	
$Cu(TTA)_2$			277			340*	
$Zn(TTA)_2$	233	265				336*	
HBTA	245				325*		
$Al(BTA)_3$		266			326*		
$Cr(BTA)_3$		269		304*			358
$Fe(BTA)_3$	256			302*			
$Mg(BTA)_2$	249				321*		
$Mn(BTA)_2$	254				326*		
$Co(BTA)_2$	253				320*		
$Ni(BTA)_2$	254		288		330*		
$Cu(BTA)_2$		272			326*		
$Zn(BTA)_2$	254				319*		
$Cd(BTA)_2$	250				323*		
$UO_2(BTA)_2$			287*		317		373

*Strongest band in spectrum.

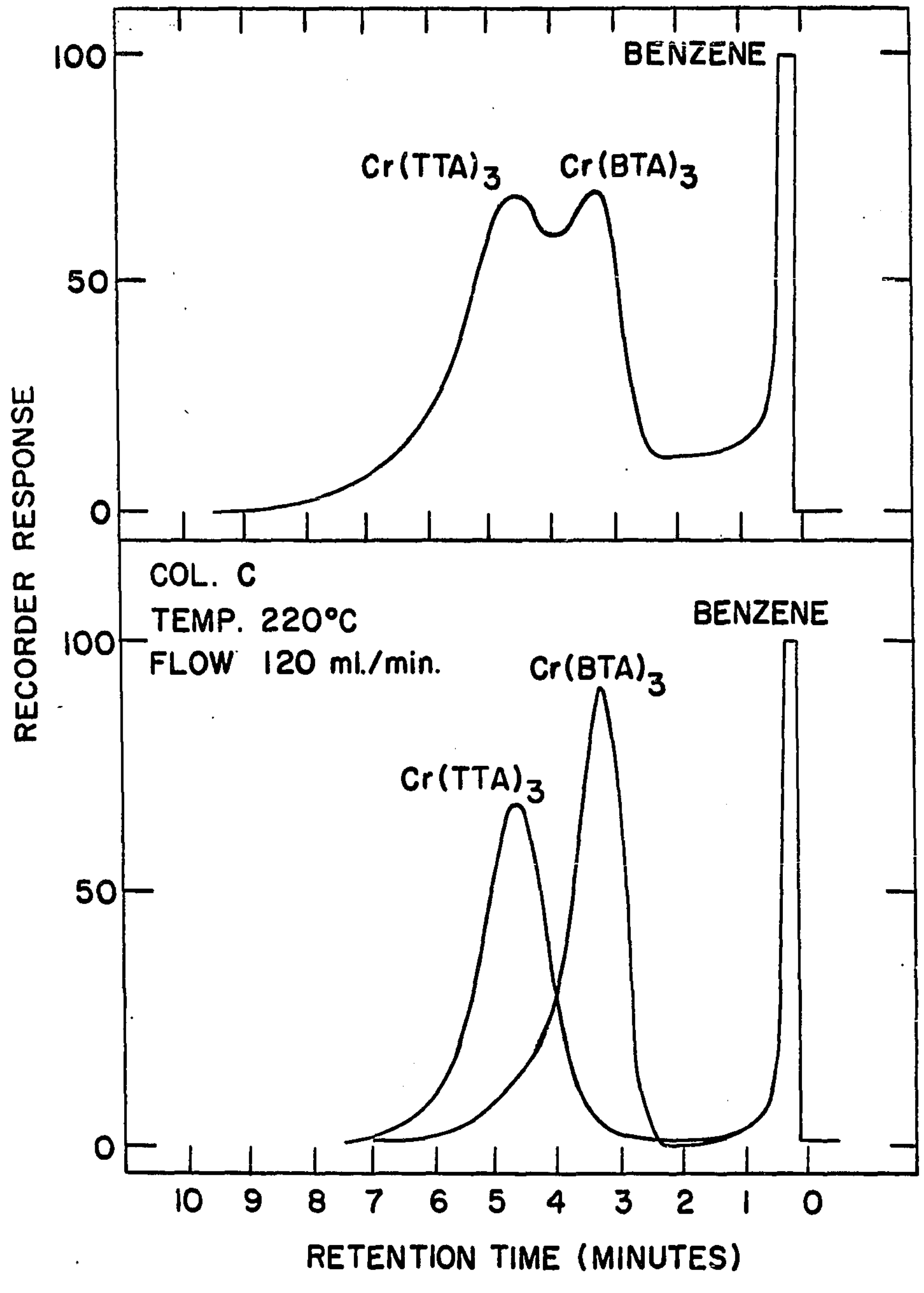

Figure 4. Gas chromatograms of a mixture of Cr(BTA)$_3$ and Cr(TTA)$_3$ and of the separate chelates

helium carrier gas when the solvent is vaporized. Consequently, much lower temperatures were required to ensure volatilization of the chelates than if they were introduced as solids.

Thermal decomposition and reaction with column materials Thermal decomposition can be an important problem in the gas chromatography of the metal chelates of HTTA and HBTA. Above about 250°C thermal degradation occurs with nearly all β-diketone chelates. This decomposition is best minimized by choosing columns which permit elution of the chelates at the lowest practical temperature.

Lightly loaded columns, columns in which the solid support is only lightly coated with liquid stationary phase, were found to be best suited for this purpose. General purpose G.C. columns usually contain 15 to 25% liquid phase; lightly loaded columns contain less than one per cent. With the lightly loaded columns, however, uncoated sites on the support are free to react with the chelate samples. Consequently, non-reactive supports such as glass beads were used.

The nature of the column material can also affect the elution of the chelates. Most chelates of HBTA and HTTA injected into columns constructed from copper tubing failed to be eluted. Stainless steel columns were little better; the chelates that were eluted generally gave very broad and distorted chromatographic peaks, and a material having a red color characteristic of the iron chelate was collected in the effluent. Sievers et al. (79) reported a similar observation for the chelates of HTFA. Apparently catalytic decomposition and/or reaction with the column material occurred. To avoid these difficulties, glass columns and glass inlet liners were employed. The transparent glass was also useful in obtaining visual evidence of decomposition or incomplete volatilization in the gas chromatographic system.

Samples of $Cr(BTA)_3$ and $Fe(BTA)_3$ were injected into the heated inlet of the chromatograph at a series of temperatures ranging from 100° to 300°C. After each injection the liner was removed and inspected for residue. The chromium chelate showed no residue between 150° and 240°C. A slight residue was present at higher temperatures indicating partial decomposition. The deposit at the lower temperatures was the result of incomplete vaporization of the chelate sample. A residue was present after each injection of $Fe(BTA)_3$, although it was slight at temperatures higher than 150°C.

Chromatograms Each component as it is eluted from the gas chromatograph produces a peak on the chromatogram which can be characterized by its shape and its retention time. The chromatograms for the copper, aluminum, gallium, and chromium chelates of HBTA are shown in Figure 5. Two-microliter samples of approximately one-tenth molar solutions of the chelates were used. The symmetrical shape of the peaks indi-

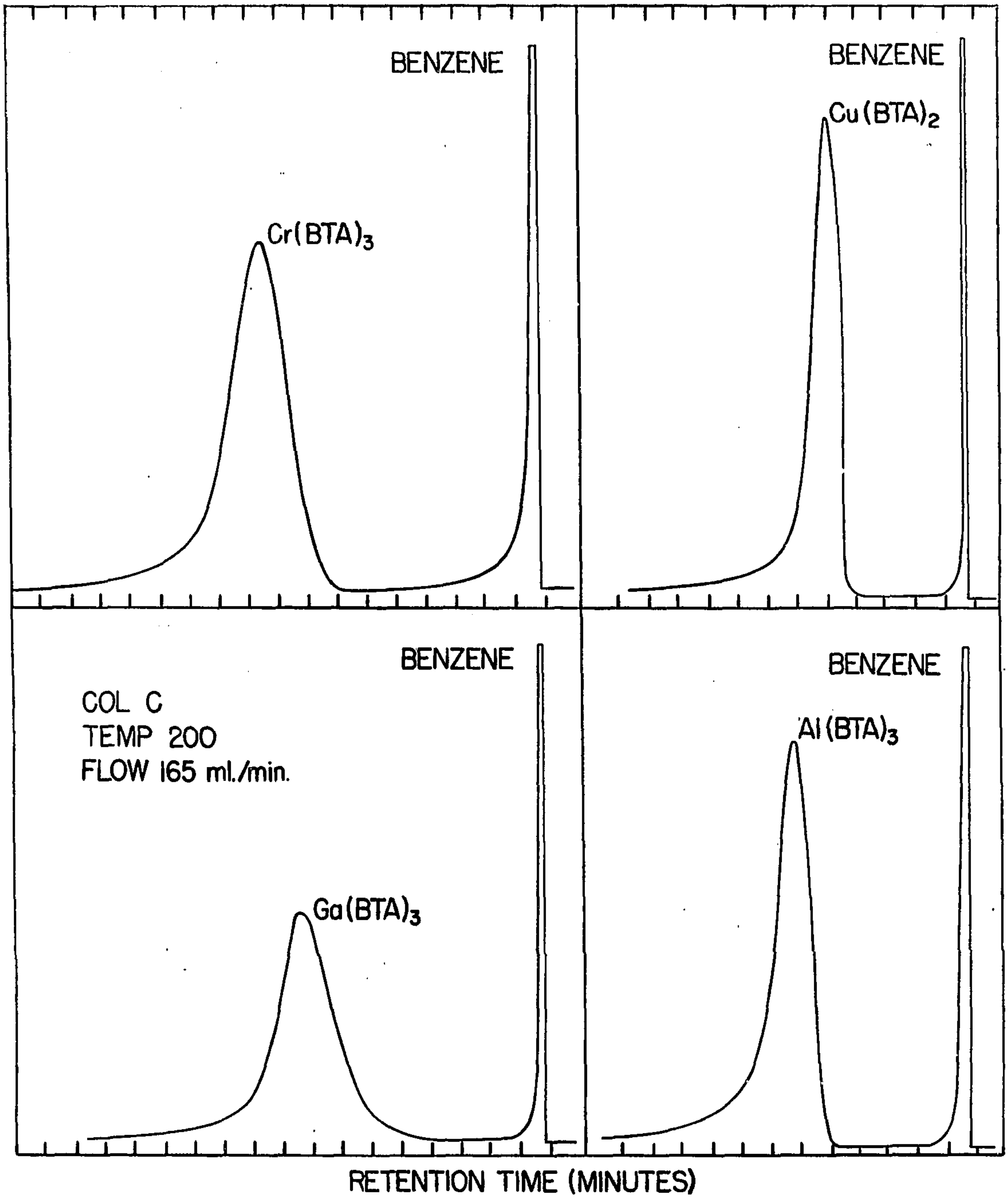

Figure 5. Gas chromatograms of Cu(BTA)$_2$, Al(BTA)$_3$, Ga(BTA)$_3$, and Cr(BTA)$_3$

cates normal chromatographic behavior, as opposed to decomposition, adsorption, or other adverse reactions. The different retention times for each chelate indicate unique species rather than a common decomposition product were eluted. As discussed earlier, the eluted species were shown to be the same as the injected chelates.

Table 7 lists the retention times for several chelates of HBTA and HTTA. Two-microliter samples of one-tenth molar chelate solutions were again employed. These data also demonstrate the greater volatility of the HBTA chelates as compared to those of HTTA. The retention time reported for $Fe(TTA)_3$ is questionable because the peak was very broad and distorted indicating decomposition. Residue in the inlet linear confirmed the occurrence of decomposition.

Table 7. Retention times for some chelates of HBTA and HTTA

Metal	Retention time (minutes)[a]	
	HBTA	HTTA
Cu	4.0	4.1
Al	5.6	6.5
Sc	6.8	--
Ga	7.4	9.8
Cr	7.9	10.0
Fe	10.7	18[b]

[a] Obtained with column C at a temperature of 200°C and a flow rate of 120 ml/min.

[b] Partial decomposition occurs.

Figure 6 illustrates the rapidity with which the chelates may be eluted. The retention time for the Al(BTA)$_3$ under the conditions shown was slightly more than one minute. Decomposition, however, can be a problem at such temperatures, even though no residue was observed in the liner.

Separations Although lightly loaded columns are useful in maintaining lower operating temperatures, they produce poorer resolution than columns with more liquid phase. Despite this low efficiency, several separations of the chelates of HBTA were accomplished. Figure 7 shows the rapid separation of Al(BTA)$_3$ and Fe(BTA)$_3$ with nearly baseline resolution. The partial resolution of four chelates of HBTA is shown in Figure 8. This chromatogram indicates that a quantitative determination of a mixture of Cu(BTA)$_2$, Al(BTA)$_3$, and Cr(BTA)$_3$ should be possible by gas chromatography.

Additional studies of the chromium chelates Additional studies were performed with the chromium chelates of HBTA and HTTA. The purposes of these studies were to determine the temperature range over which the chelates could be chromatographed, separate geometrical isomers of the chelates, and evaluate the concentration range in which the chelates could be quantitatively chromatographed. Chromium chelates were chosen for this study because the gas chromatography of the chromium chelates of other β-diketones is well documented and available for comparison.

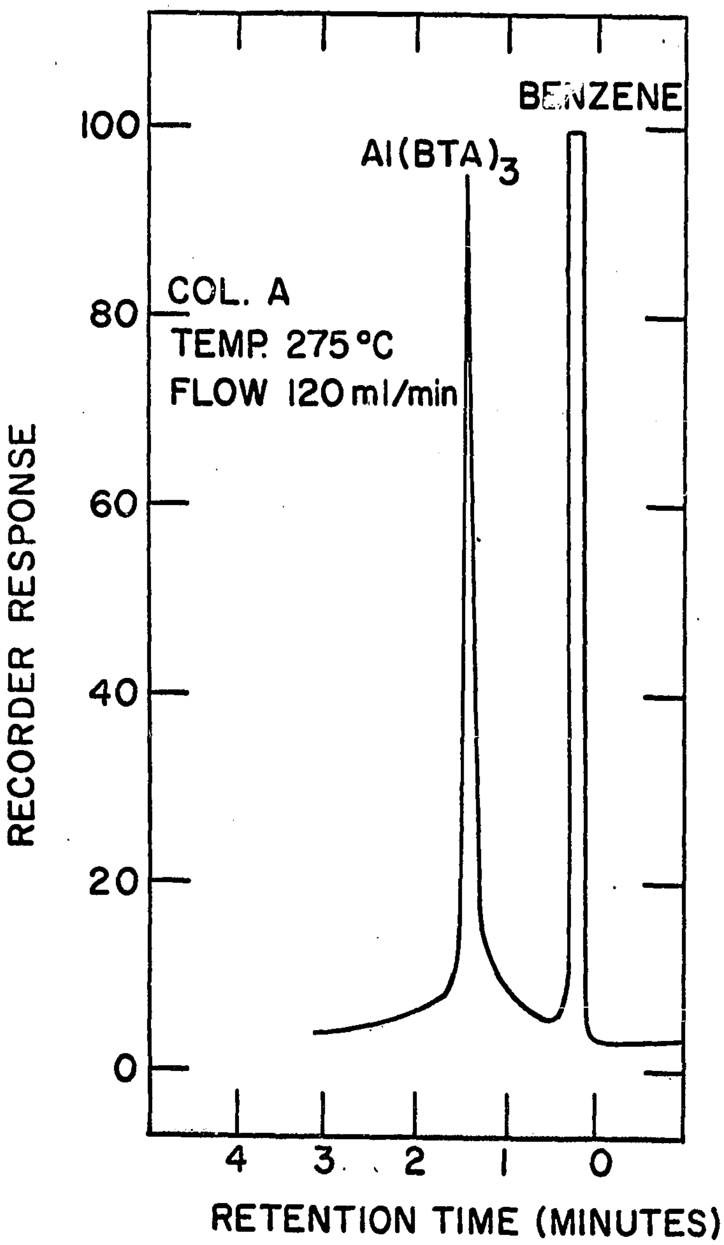

Figure 6. Gas chromatogram of $Al(BTA)_3$

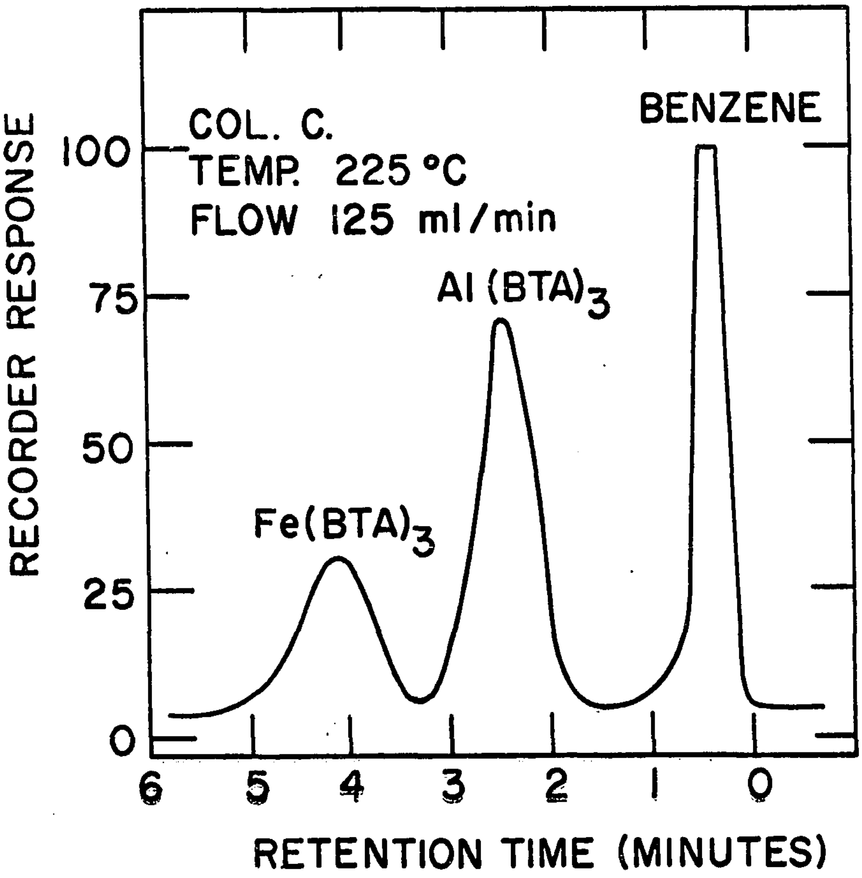

Figure 7. Gas chromatogram of a mixture of $Al(BTA)_3$ and $Fe(BTA)_3$

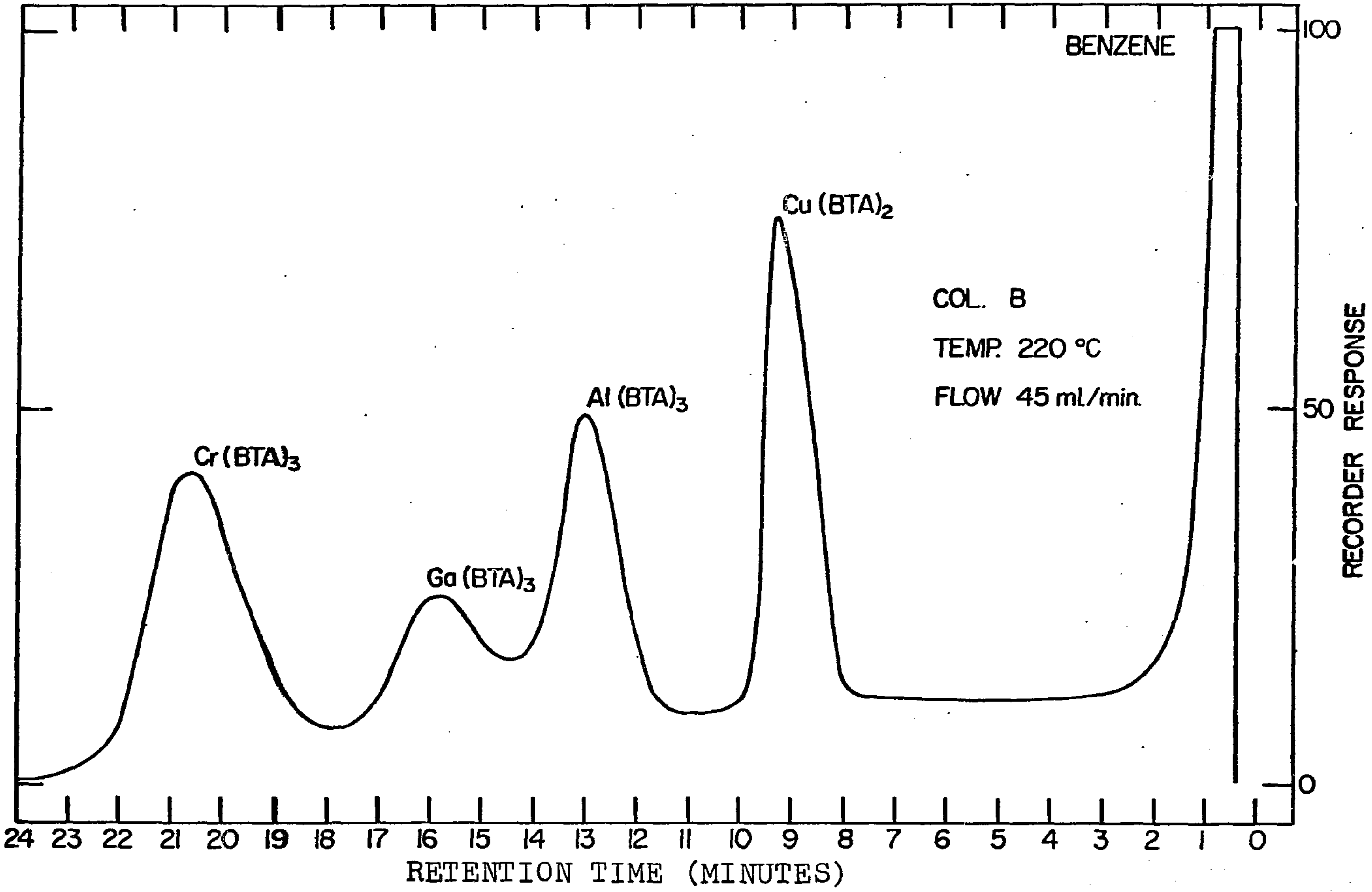

Figure 8. Gas chromatogram of a mixture of $Cu(BTA)_2$, $Al(BTA)_3$, $Ga(BTA)_3$, and $Cr(BTA)_3$

Retention dependence on temperature Dal Nogare and Juvet (22, p. 79) have derived the expression

$$\log V_g = -\Delta H_s/(2.3\ R\ T) + C,$$

where V_g is the specific retention volume of an eluted compound, ΔH_s is the heat of solution of the solute-liquid phase combination, and T is the absolute temperature of the chromatographic column. Figure 9 shows plots of the logarithm of the measured retention time (t_r), which is directly related to V_g (22), versus reciprocal temperature for $Cr(BTA)_3$ and $Cr(TTA)_3$. The data for this figure are included in Table 8. The linearity of the plots is further confirmation of normal chromatographic behavior by these chelates. Although the thermodynamic values obtainable in this case are not pertinent because the liquid phase is silicone oil, Cartoni (16) using inverse gas chromatography with the chelates as the stationary phase has obtained solubility data for several β-diketone chelate-organic solvent systems.

Table 8. Retention time and temperature data for $Cr(BTA)_3$ and $Cr(TTA)_3$

Temperature		Retention time (minutes)[a]	
°K	°C	$Cr(BTA)_3$	$Cr(TTA)_3$
503	230	1.88	3.04
493	220	3.20	4.92
483	210	5.52	8.60
463	190	16.4	26.7
453	180	28.2	45.3
443	170	50.8	--

[a] Obtained with column C at a flow rate of 120 ml/min.

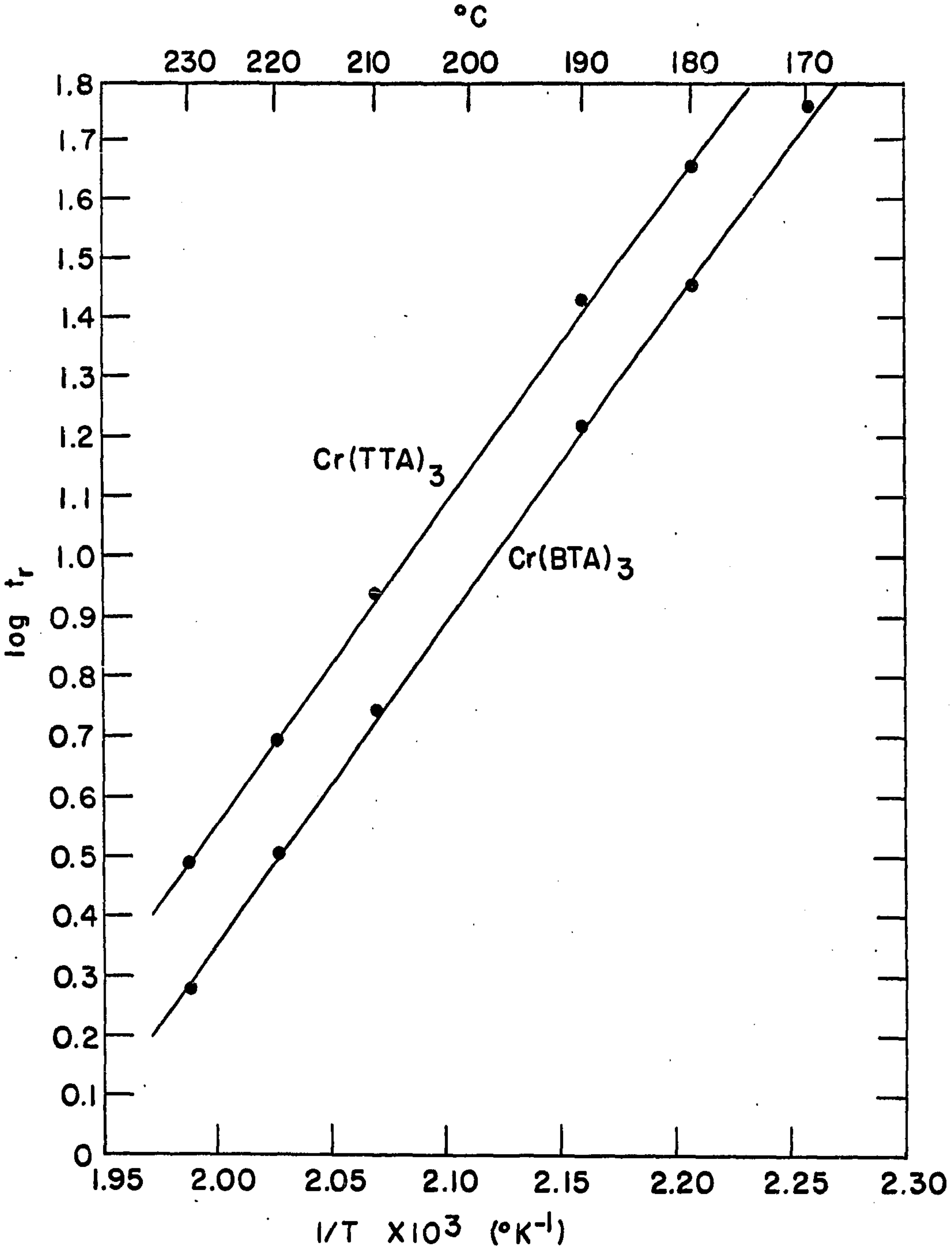

Figure 9. Dependence of the logarithm of the retention time, t_r, on column temperature for Cr(BTA)$_3$ and Cr(TTA)$_3$

Isomers of $Cr(BTA)_3$ The existence of geometrical isomers is possible for octahedral complexes of unsymmetrical bidentate ligands such as HTFA, HBTA, and HTTA. Figure 10 shows the necessary configurations of the *cis* and *trans* isomers. Note that in the *cis* isomer, the "A" groups are all on the same side of the molecule. This should cause the *cis* isomer to be more polar and less volatile than the *trans* isomer. Gas chromatographic separations of the geometrical isomers of $Cr(TFA)_3$ in which the *trans* isomer was eluted first has been accomplished by Sievers *et al.* (79).

The apparent partial resolution of the isomers of $Cr(BTA)_3$ was achieved as indicated in Figure 11. This chromatogram was obtained with a saturated solution of $Cr(BTA)_3$ in benzene. The column employed was both longer and more highly loaded than those used for the other studies of the HBTA chelates[1]. Complete separation of these isomers may not be possible because of increased isomerization at elevated temperatures (26,27,28). Only the gas chromatographic separation of the isomers of inert complexes of chromium (79) and rhodium (62) have been reported. Labile complexes of elements such as aluminum and iron apparently rearrange too rapidly to be isolated (20,26,27,42).

Quantitative studies Analytical curves were prepared for both $Cr(TTA)_3$ and $Cr(BTA)_3$. The solutions used for

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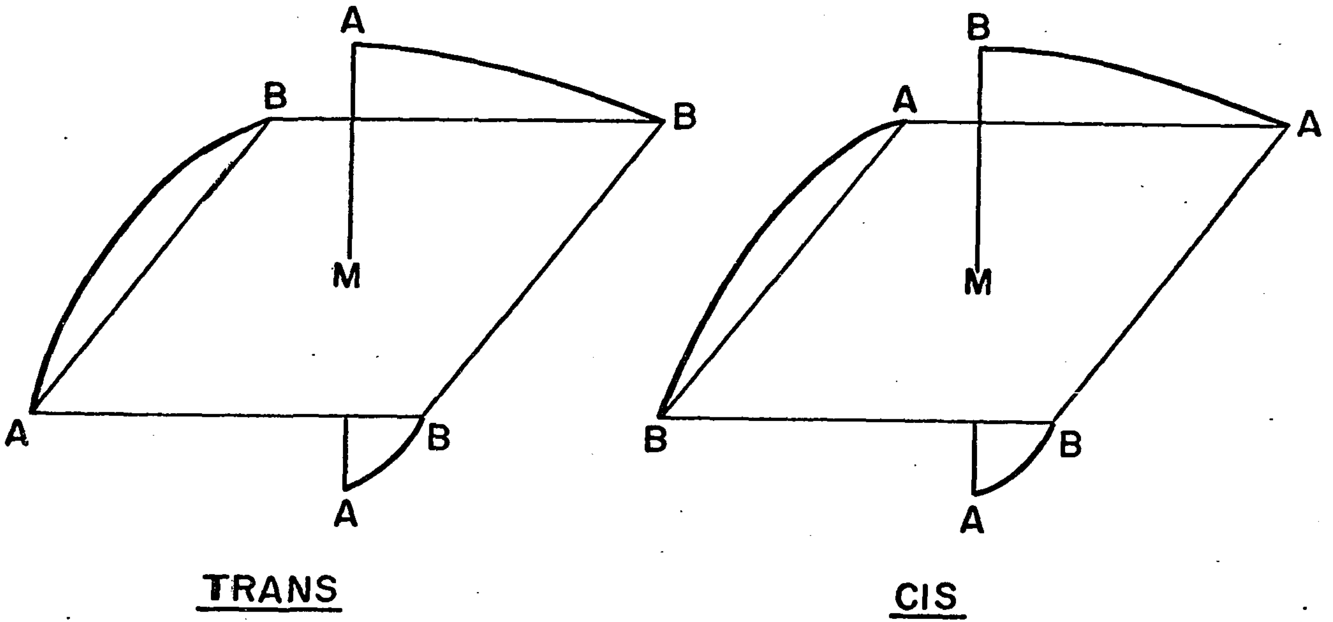
[1] See APPENDIX B for a listing of columns.



TRANS

CIS

Figure 10. Schematic representation of the <u>trans</u> and <u>cis</u> configurations of geometrical isomers of octahedral complexes of unsymmetrical bidentate ligands

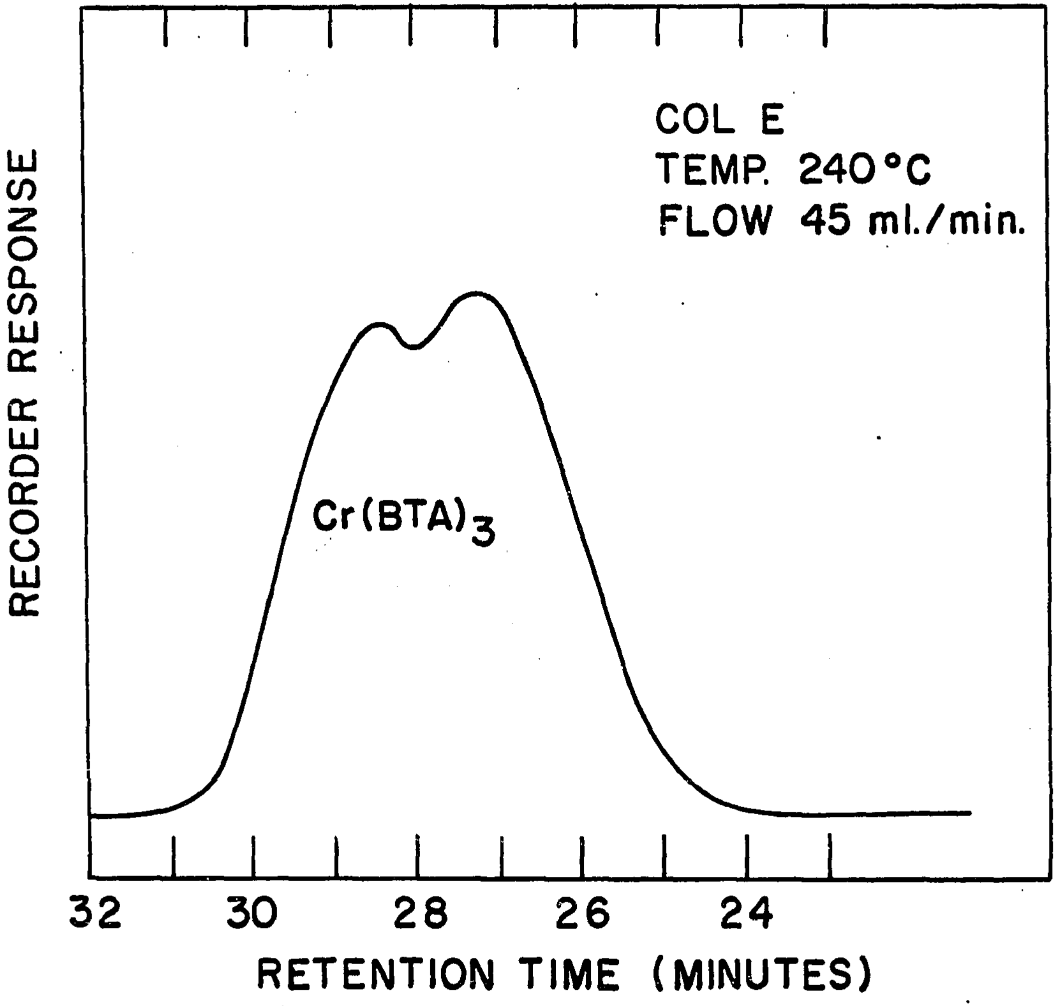


Figure 11. Gas chromatogram of apparent partial resolution of geometrical isomers of $Cr(BTA)_3$

these curves were a series of dilutions of a standard solution prepared from the purified solid chelate. The results are shown in Figures 12 and 13. Tables 9 and 10 contain the data for these plots.

Table 9. Concentration and peak height data for $Cr(TTA)_3$

$[Cr(TTA)_3]$[a]	Attenuation	Measured peak height (mm)[b,c]	Relative peak height
2.90×10^{-2}	2×10^3	61.0 ± 3.5	1.22×10^5
2.32×10^{-2}	1×10^3	88.4 ± 3.1	8.84×10^4
1.45×10^{-2}	1×10^3	44.3 ± 0.4	4.43×10^4
7.25×10^{-3}	5×10^2	23.5 ± 1.0	1.18×10^4
3.63×10^{-3}	2×10^2	14.0 ± 0.7	2.80×10^3

[a] Benzene solvent.

[b] Average deviations for four determinations given with measured peak height.

[c] Obtained with column C at a temperature of 230°C and a flow rate of 120 ml/min.

The curve for $Cr(BTA)_3$ is linear over a much greater range than that for $Cr(TTA)_3$. The lower concentration limit of these analytical curves was restricted by the sensitivity of the detector in the case of $Cr(BTA)_3$ and by the noise level for $Cr(TTA)_3$. The relatively high concentration at which the signal-to-noise ratio was insufficient for quantitative results indicates partial decomposition of the chromium chelate of HTTA.

One-microliter samples were used throughout the quantitative studies. The amount of chromium contained in the most dilute $Cr(BTA)_3$ sample was, therefore, 3.4×10^{-9} gram.

Table 10. Concentration and peak height data for $Cr(BTA)_3$

$[Cr(BTA)_3]^a$	Attenuation	Measured peak height (mm)^{b,c}	Relative peak height
3.34×10^{-2}	5×10^3	26.4 ± 1.7	1.32×10^5
1.67×10^{-2}	2×10^3	27.0 ± 0.8	5.40×10^4
8.35×10^{-3}	1×10^3	22.0 ± 0.8	2.20×10^4
4.18×10^{-3}	5×10^2	18.0 ± 0.7	9.00×10^3
2.09×10^{-3}	2×10^2	17.7 ± 1.1	3.54×10^3
1.05×10^{-3}	1×10^2	14.9 ± 2.0	1.49×10^3
5.25×10^{-4}	5×10	14.0 ± 0.7	7.00×10^2
2.62×10^{-4}	2×10	15.7 ± 1.1	3.14×10^2
1.31×10^{-4}	1×10	18.0 ± 1.0	1.80×10^2
6.55×10^{-5}	1×10	10.1 ± 1.5	1.01×10^2

[a] Benzene solvent.

[b] Average deviations for four determinations given with measured peak height.

[c] Obtained with column C at a temperature of 210°C and a flow rate of 120 ml/min.

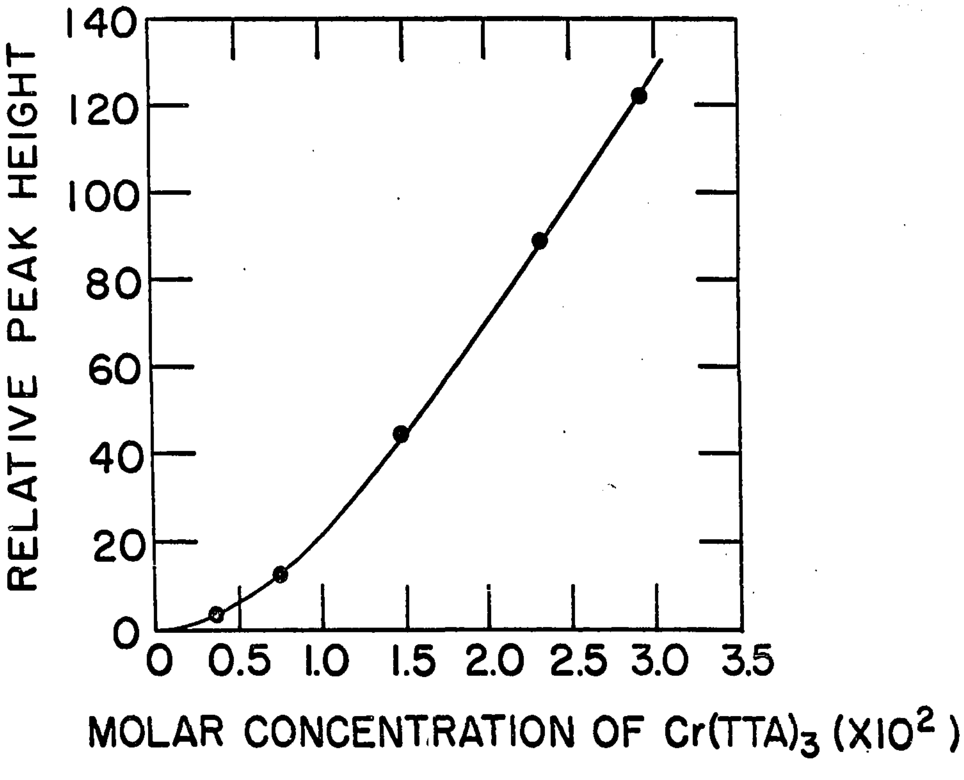


Figure 12. Relative peak height as a function of the concentration of $Cr(TTA)_3$

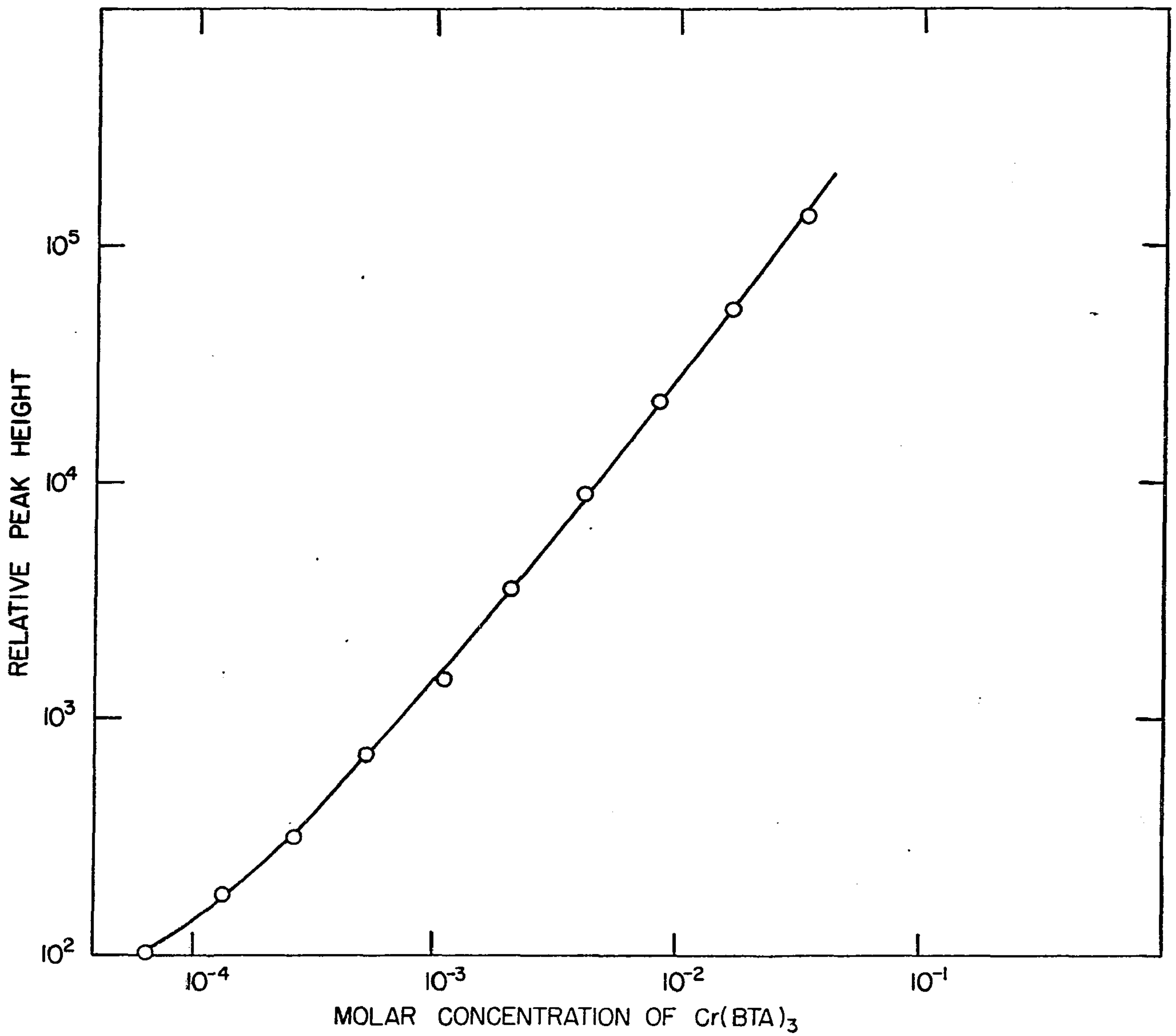


Figure 13. Relative peak height as a function of the concentration of $Cr(BTA)_3$

Mixed-ligand complexes With the exception of divalent copper, only the gas chromatography of the chelates of HBTA and HTTA with the trivalent metals has been discussed to this point. The trivalent transition metals and copper(II) were the only metal ions investigated that formed chelates sufficiently soluble in an organic solvent to be sampled for gas chromatographic studies. These were also the only chelates that were analyzed and found to be anhydrous. Apparently hydration is largely responsible for the decreased solubility of the other chelates. Other workers (79,65) have encountered the same occurrence with chelates of HACAC, HTFA, and HHFA and have prepared anhydrous chelates by the use of desiccants and heating at reduced pressure. These anhydrous chelates were more soluble in organic solvents and generally gas chromatographable. A similar study was not undertaken as part of this project because the hydrated species are formed during attempted solvent extraction and do not extract sufficiently for gas chromatographic applications (69).

The use of mixed ligands to extract such metal ions has already been discussed. Schribner and Kotecki (68) described the use of HTFA and isobutylamine to extract the mixed-ligand complexes of divalent nickel, copper, cobalt, zinc, and cadmium. They also reported that some of these complexes were successfully gas chromatographed.

Mixed-ligand complexes of HTTA (15) and of HBTA (57,75) have been shown to possess much larger distribution ratios than the corresponding simple chelates. This synergic effect is greatest for those complexes in which the neutral adduct replaces water in the coordination sphere.

Solid samples of $Cu(BTA)_2$ and $Zn(BTA)_2 \cdot H_2O$ were dissolved in benzene in the presence of TBP or n-butylamine. Both neutral adducts increased the solubility of the chelates, particularly that of the zinc chelate. The resultant solutions were gas chromatographed with the results shown in Table 11.

Table 11. Retention times of some complexes formed by extraction with HBTA and a neutral adduct

Metal	Adduct	Retention time (minutes)[a]
Cu	--	0.60
Cu	n-butylamine	0.68
Zn	--	2.36
Zn	n-butylamine	2.52
Zn	TBP	2.58

[a] Obtained with column H at a temperature of 220°C and a flow rate of 50 ml/min.

The anhydrous zinc chelate was prepared by heating a sample of $Zn(BTA)_2 \cdot H_2O$ at 110°C for two hours. The chromatographic peaks were sharp and well defined, similar to that shown for $Cu(BTA)_2$ in Figure 5. The retention times for the mixed-ligand complexes were slightly greater than those for the simple chelates indicating that the species being chromatographed was either the heavier mixed ligand complex or a decomposition product. The most likely decomposition product would be the anhydrous chelate, the elution of which was delayed by the breakdown of the mixed complex. In either case, this experiment demonstrates the feasibility of obtaining gas chromatograms for complexes of metal ions that cannot be extracted and chromatographed as simple chelates.

Conclusions

The most obvious conclusion to be drawn from the preceding studies is that HBTA is a much more suitable ligand than HTTA for forming gas chromatographable metal chelates. The extraction properties of the two ligands are nearly identical, and the chelates of HBTA are significantly more volatile. Because of the higher operating temperatures required for the gas chromatography of the HTTA chelates, decomposition would be a definite problem in attempts to develop an analytical technique employing the gas chromatography of chelates of this ligand.

Although HBTA forms chelates that are sufficiently volatile to avoid operating temperatures that are likely to cause decomposition, relatively high column temperatures are still required. This requirement of operating temperatures near 200°C places a restriction on the choice of column packing and column length and, as a result, limits the efficiency of the columns that can be used. The potential application of the extraction and gas chromatography of chelates of HBTA appears to be limited to metal ions which cannot be adequately extracted by ligands, such as HTFA and HHFA, which form more volatile chelates.

INVESTIGATION OF THE MIXED LIGANDS HHFA AND TBP AS A GAS CHROMATOGRAPHIC REAGENT FOR THE RARE EARTHS

Results and Discussion

Hexafluoroacetylacetone was chosen as the β-diketone for this study because of the extreme volatility of its chelates (10,19,32,78,79). The synergic extractions of several metals with HHFA and tri-n-octylphosphine oxide have been demonstrated (17,45,89); therefore, other organophosphorus neutral adducts were expected to exhibit similar synergism. The adducts chosen for consideration were tri-n-butylphosphine oxide[1] (TBPO) and tri-n-butylphosphate (TBP). The butyl alkyl group was a compromise between a larger group expected to form complexes with greater distribution ratios and a smaller group expected to form more volatile complexes.

Burger (14) has found the organophosphates to be more volatile than the phosphine oxides and explained this on the basis of the greater polarity of the phosphine oxides. This same trend was observed for the complexes of HHFA with TBPO and TBP as shown in Table 12. In addition to the greater volatility of the TBP complexes, another reason for using TBP in preference to TBPO is illustrated in Figure 14. Figure 14B is a chromatogram of TBPO in cyclohexane, represented by the two tall peaks. It is obvious that the ligand is either

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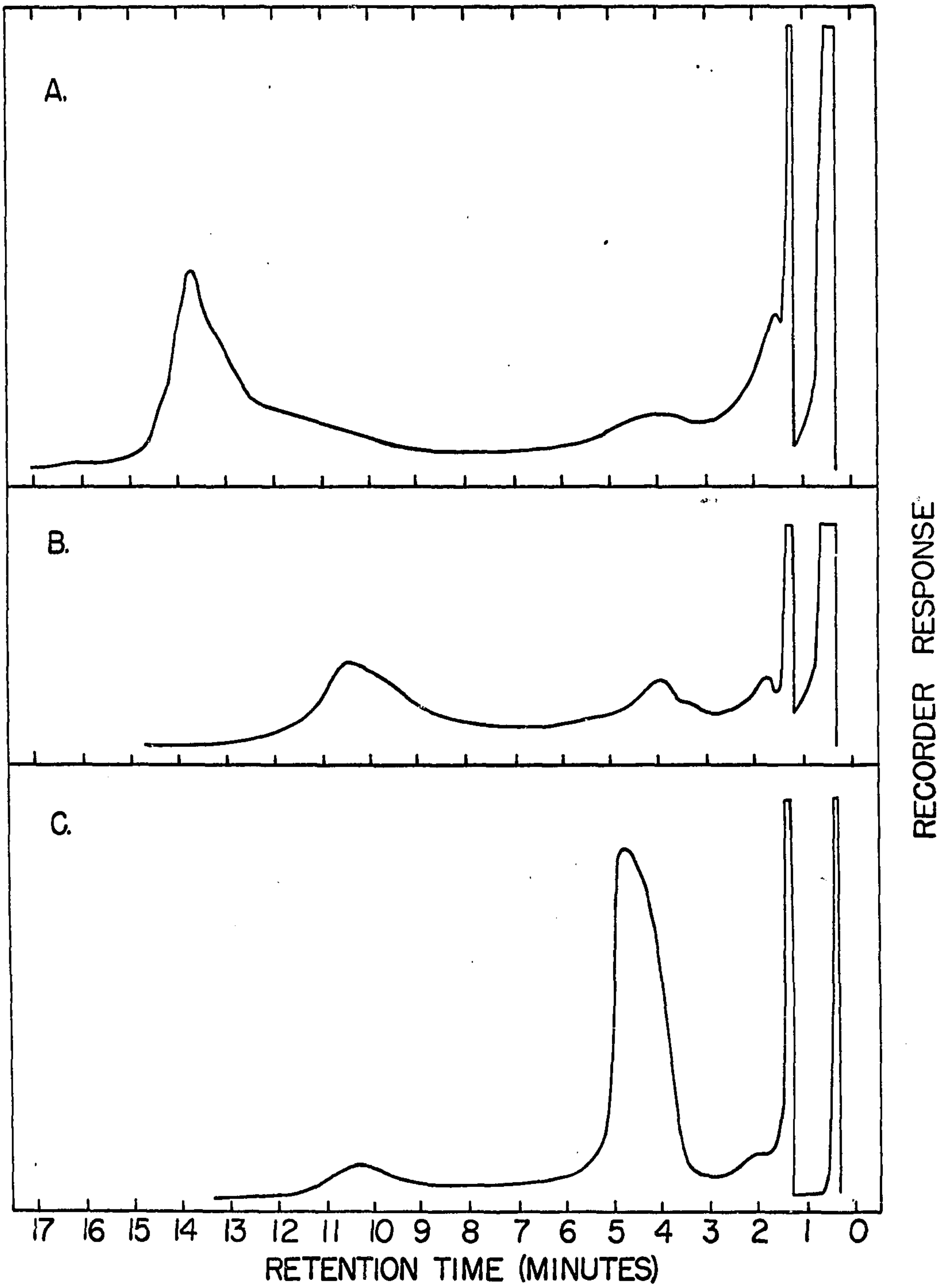
[1] See APPENDIX A for structure and nomenclature of ligands.

Figure 14. Gas chromatograms of: A. Cyclohexane phase from an extraction of Eu^{+3} with HHFA and TBPO, B. Cyclohexane solution of TBPO, C. Cyclohexane phase from an extraction of Yb^{+3} with HHFA and TBPO


A.
B.
C.
RECORDER RESPONSE
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
RETENTION TIME (MINUTES)

impure or decomposes. The chromatograms of the europium and ytterbium complexes show similar spurious peaks as well as distortion of the peaks attributed to the complexes. The chromatograms of the mixed-ligand complexes of HHFA and TBP are much cleaner and better defined, as will be shown.

Table 12. Retention times for some mixed-ligand complexes with HHFA and TBP or TBPO

Complex	Retention time (minutes)[a] TBP	TBPO
Pure ligand	0.6	1.0
Yb complex	1.4	4.3
Eu complex	3.1	12.0

[a] Obtained on column I at a temperature of 190°C and a flow rate of 55 ml/min.

Gas chromatography of complexes

All of the samples of the metal complexes of HHFA and TBP used in the following gas chromatographic studies were taken from the cyclohexane phase of extractions with HHFA and TBP. The extraction technique was previously outlined in the section EXPERIMENTAL PROCEDURES. A flame ionization detector was used throughout this study. Unless indicated otherwise, the sample concentrations are approximately 0.01 molar in each rare earth complex present in the sample solution.

Chromatograms Gas chromatograms of the HHFA and TBP mixed-ligand complexes of yttrium and of all the rare earths, except promethium, were obtained and are shown in Figures 15 and 16. These chromatograms were not all obtained at the same temperature because the differences in the volatilities of the complexes were too large to obtain practical chromatograms at a common temperature. It is apparent, however, that useful chromatograms of the HHFA and TBP mixed-ligand complexes of all of the rare earths can be obtained. The "leading" exhibited by some of the chromatograms in Figure 16 is probably attributable to thermal decomposition and is discussed in the next section.

The retention times of samples eluted from a gas chromatographic column are frequently dependent on the sample size (22, p. 170). To compare the retention times of different samples it is necessary to extrapolate the retention times to zero sample size. This was done for the rare earth complexes of the mixed ligands HHFA and TBP as shown in Figure 17. The zero sample retention times are summarized in Table 13.

A plot of the zero sample retention time versus the ionic radius of the corresponding trivalent rare earth gives the results shown in Figure 18. The complex of yttrium appears in approximately the proper position on the basis of trivalent ionic radius despite its much smaller mass. The decrease in radius with an increase in mass of the rare earth is a result of the lanthanide contraction. Other workers

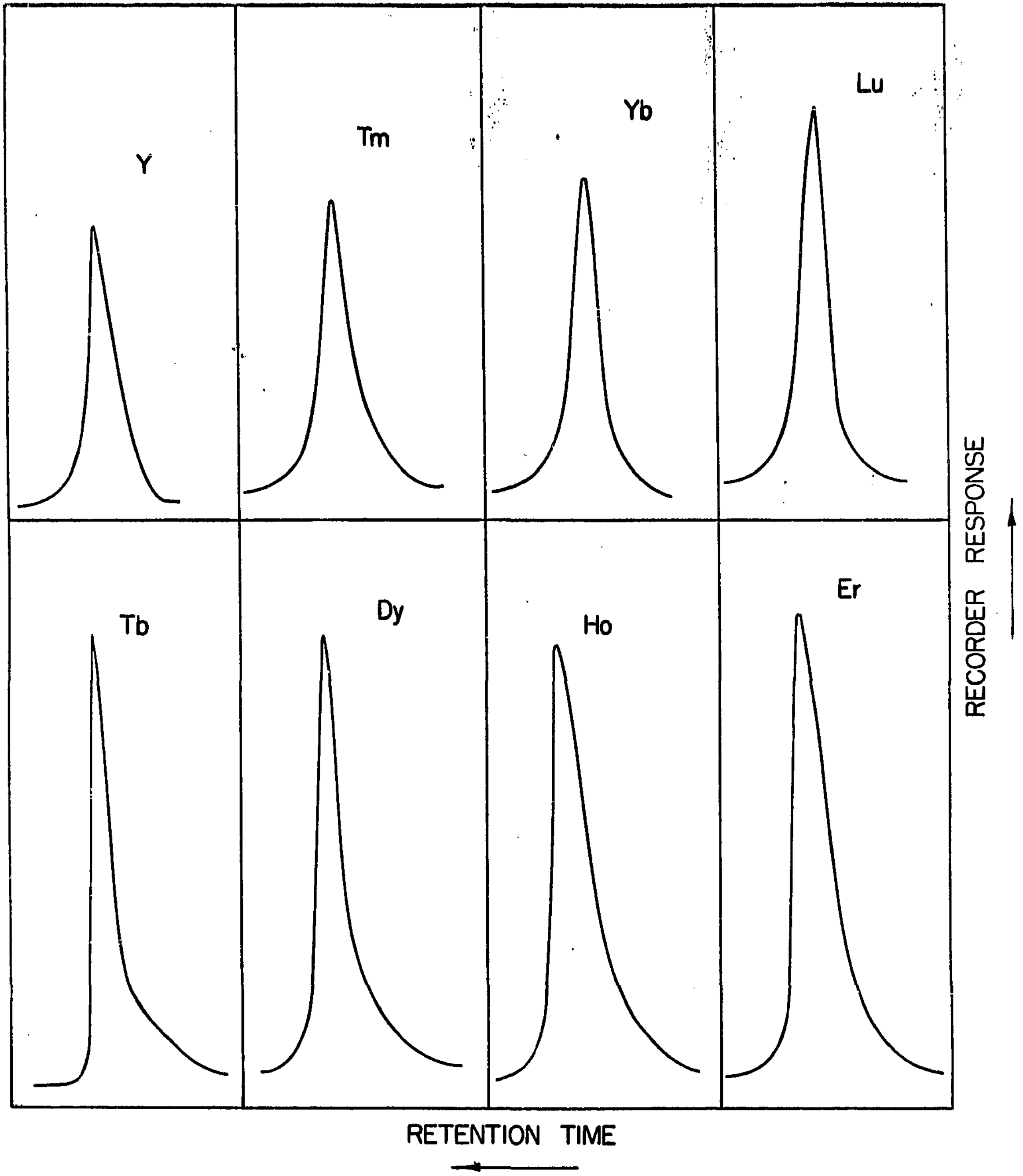


Figure 15. Gas chromatographic peaks for the HHFA and TBP mixed-ligand complexes of some rare earths and yttrium

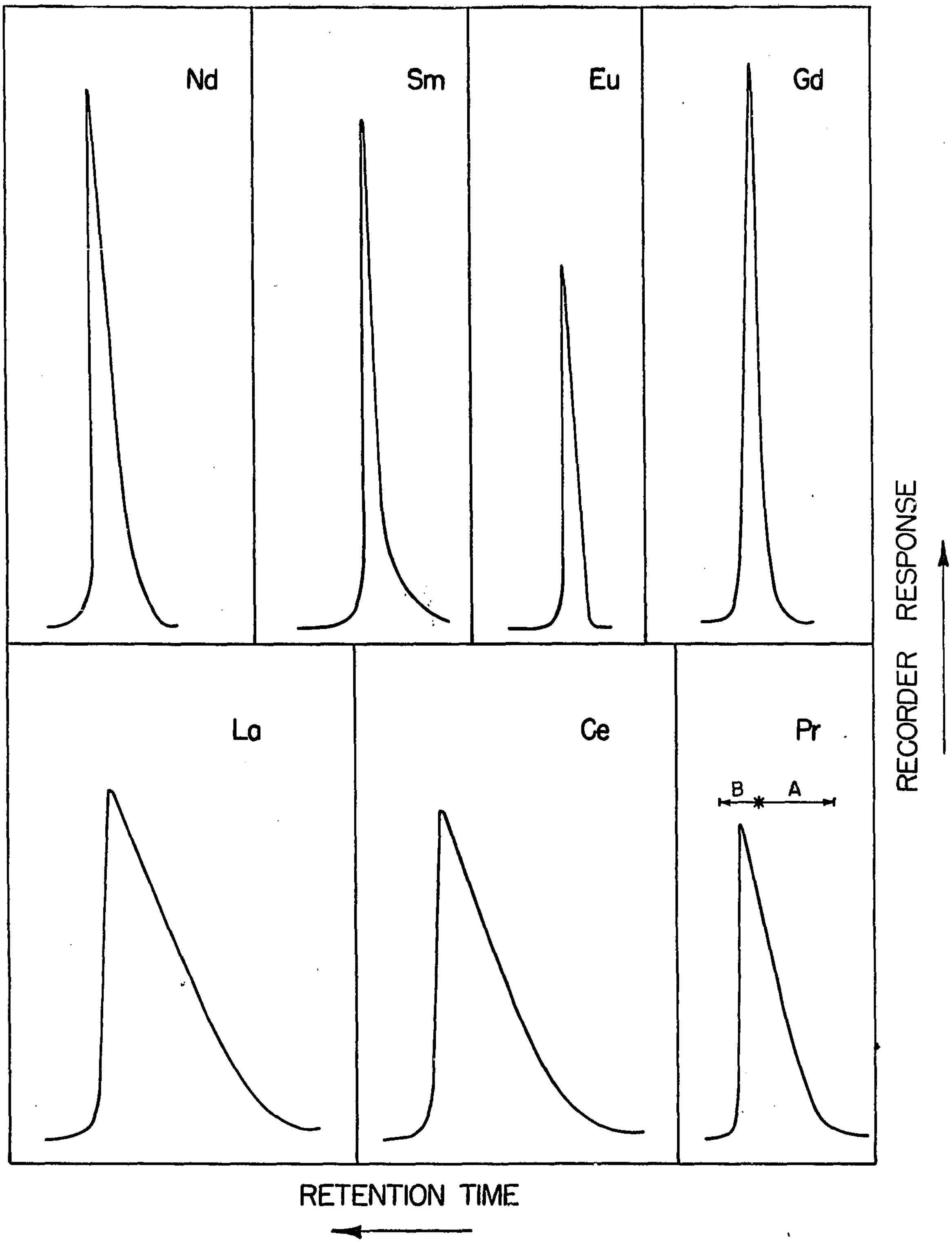


Figure 16. Gas chromatographic peaks for the HHFA and TBP mixed-ligand complexes of some rare earths

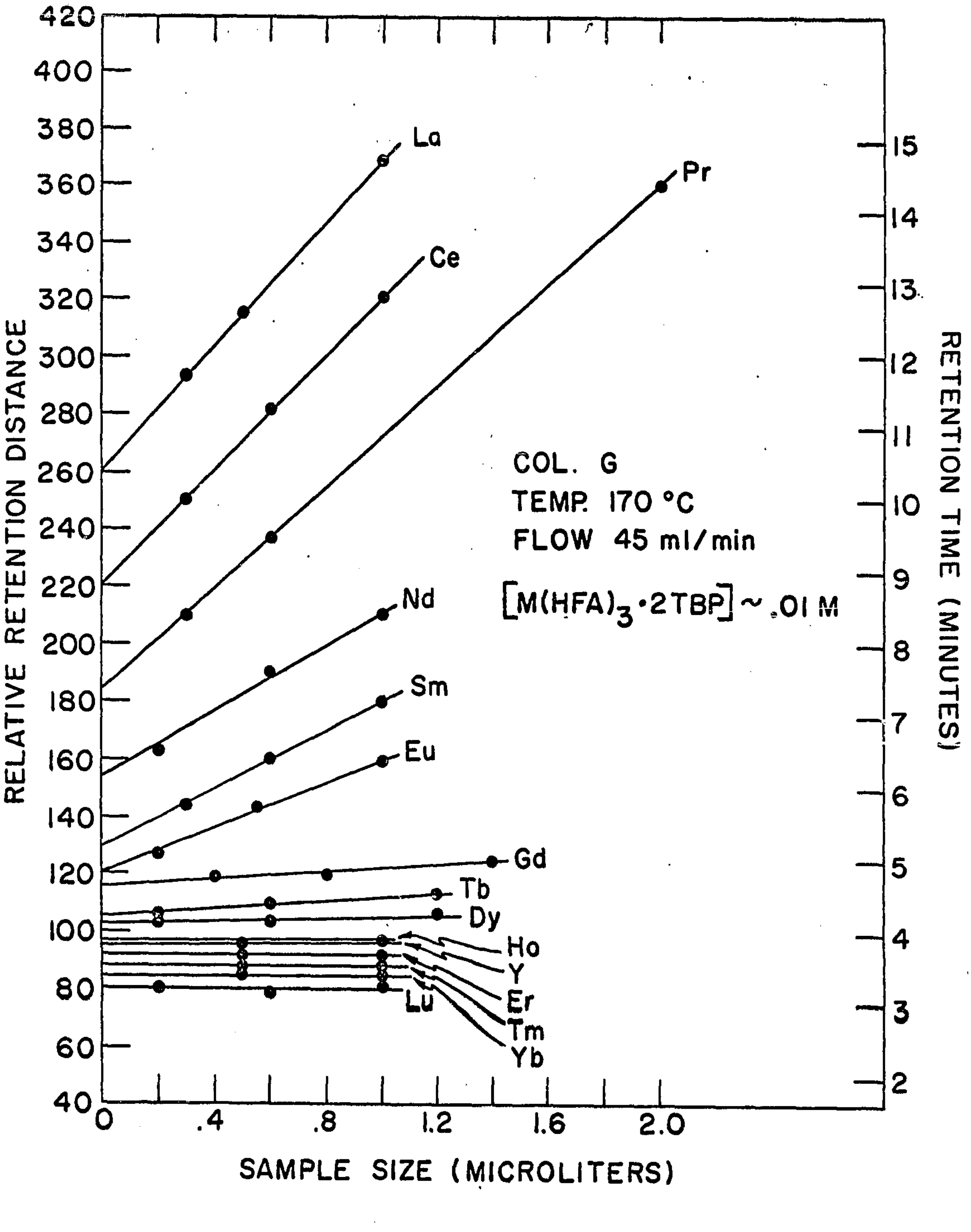
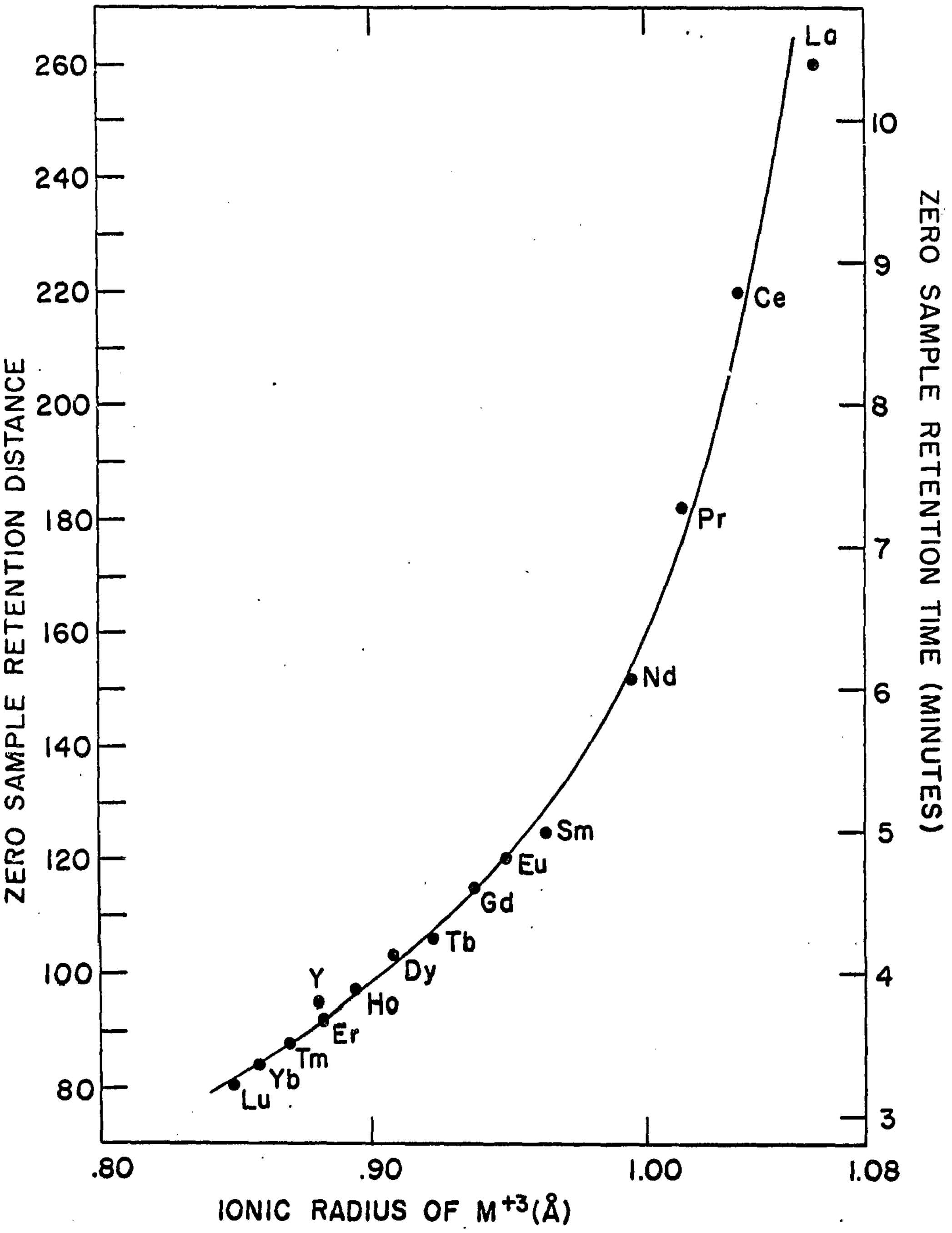


Figure 17. Dependence of retention distance and retention time on sample size for the HHFA and TBP mixed-ligand complexes of the rare earths and yttrium

Figure 18. Dependence of zero sample retention distance and zero sample retention time on the trivalent ionic radius of the complexed metal for the HHFA and TBP mixed-ligand complexes of the rare earths and yttrium


ZERO SAMPLE RETENTION DISTANCE
260
240
220
200
180
160
140
120
100
80
ZERO SAMPLE RETENTION TIME (MINUTES)
10
9
8
7
6
5
4
3
IONIC RADIUS OF M+3(Å)
.80
.90
1.00
1.08
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Y
Er
Tm
Yb
Lu

(24,81) have reported similar results with the chelates of the rare earths with HFOD and HPIV. Springer (81) attributes the increase in volatility with a decrease in the radius to a reduction in the size of the molecular and local dipoles of the complexes and to reduced polarizability.

Table 13. Zero sample retention distances and retention times for the complexes of the rare earths with the mixed ligands HHFA and TBP

Rare earth complex	Radius (A°)[a] of M^{+3}	d_{ro}(mm)[b]	t_{ro}(min)[b]
Lu	0.848	80	3.20
Yb	0.858	84	3.36
Tm	0.869	88	3.52
Er	0.881	92	3.68
Y	0.88	95	3.80
Ho	0.894	97	3.88
Dy	0.908	102	4.08
Tb	0.923	106	4.24
Gd	0.938	114	4.56
Eu	0.950	120	4.80
Sm	0.964	130	5.20
Nd	0.995	144	5.76
Pr	1.013	184	7.36
Ce	1.034	220	8.80
La	1.061	260	10.40

[a] As reported by Templeton and Dauben (86).

[b] Obtained with column G at a temperature of 170°C and a flow rate of 45 ml/min.

Thermal decomposition Glass columns and glass inlet liners were used in the study of the rare earth complexes of HHFA and TBP as in the study of the chelates of HBTA and HTTA. The liners showed no trace of residue for any of the complexes of the rare earths. The less volatile complexes, however, gave skewed peaks in their chromatograms indicating decomposition or other reaction. The praseodymium complex was chosen as typical of those with "leading" chromatographic peaks. An eluted sample was collected in two fractions as indicated on the chromatogram of the complex of praseodymium in Figure 16. Infrared spectra of the two fractions showed that the first fraction eluted was deficient in TBP. The difference in TBP content was not great, but does indicate that partial decomposition occurred. A similar study for the complex of europium indicated no decomposition took place. The data for the complex of praseodymium is given in Table 14. Complete assignments for the infrared spectra of the complexes of the rare earths with HHFA and TBP are given in a later section.

Table 14. Relative band intensities for infrared spectra of G.C. eluent fractions of $Pr(HFA)_3 \cdot 2TBP$

Wavelength (cm^{-1})[a]	Assignment	Relative band intensity A[b]	 B[c]
2976	TBP	0.42	0.52
1657	HFA	1.00	1.00
1506	HFA	0.54	0.51
1255	HFA	1.24	1.27
1040	TBP	0.67	0.76

[a] See Figure 27.

[b] Front half of peak, see Figure 16.

[c] Back half of peak, see Figure 16.

Separations Figure 19 illustrates different degrees of separation possible by the gas chromatography of HHFA and TBP mixed-ligand complexes of the rare earths. The chromatograms shown are examples of the separation of complexes of rare earths once, twice, and thrice removed from each other in the series of lanthanide elements. Figure 20 is a chromatogram of the complexes of rare earths appearing in alternate positions in the lanthanide series, and the four rare earths whose HHFA-TBP mixed-ligand complexes are partially separated in the chromatogram in Figure 21 are the last four consecutive members of the lanthanide series. This chromatogram, although unsuitable for quantitative purposes, illustrates a possible qualitative application of this technique. The chromatograms in Figure 22 illustrate the speed with which less difficult samples can be separated. Mixtures of $Yb(HFA)_3 \cdot 2TBP$ and $Eu(HFA)_3 \cdot 2TBP$ and of $Eu(HFA)_3 \cdot 2TBP$ and $Nd(HFA)_3 \cdot 2TBP$ were resolved to nearly the baseline in about five minutes. The samples for all of these separations were obtained by extraction as outlined previously.

Retention dependence on temperature The temperature dependence of the retention times for $Lu(HFA)_3 \cdot 2TBP$ and $Tm(HFA)_3 \cdot 2TBP$ are shown in Table 15 and Figure 23. The significance of a plot of the logarithm of the retention time versus the reciprocal temperature was discussed on page 37. The pertinent aspects of these data are the linearity of the

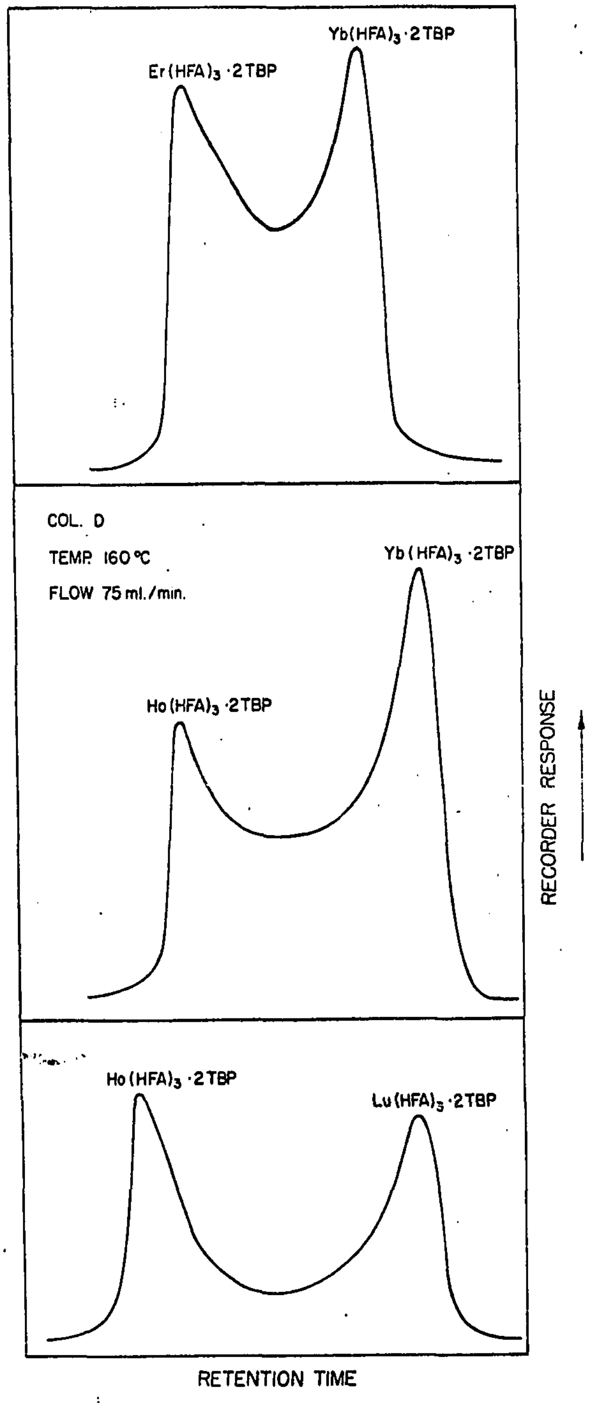


Figure 19. Gas chromatograms for some two component mixtures of some rare earth complexes of the mixed ligands HHFA and TBP

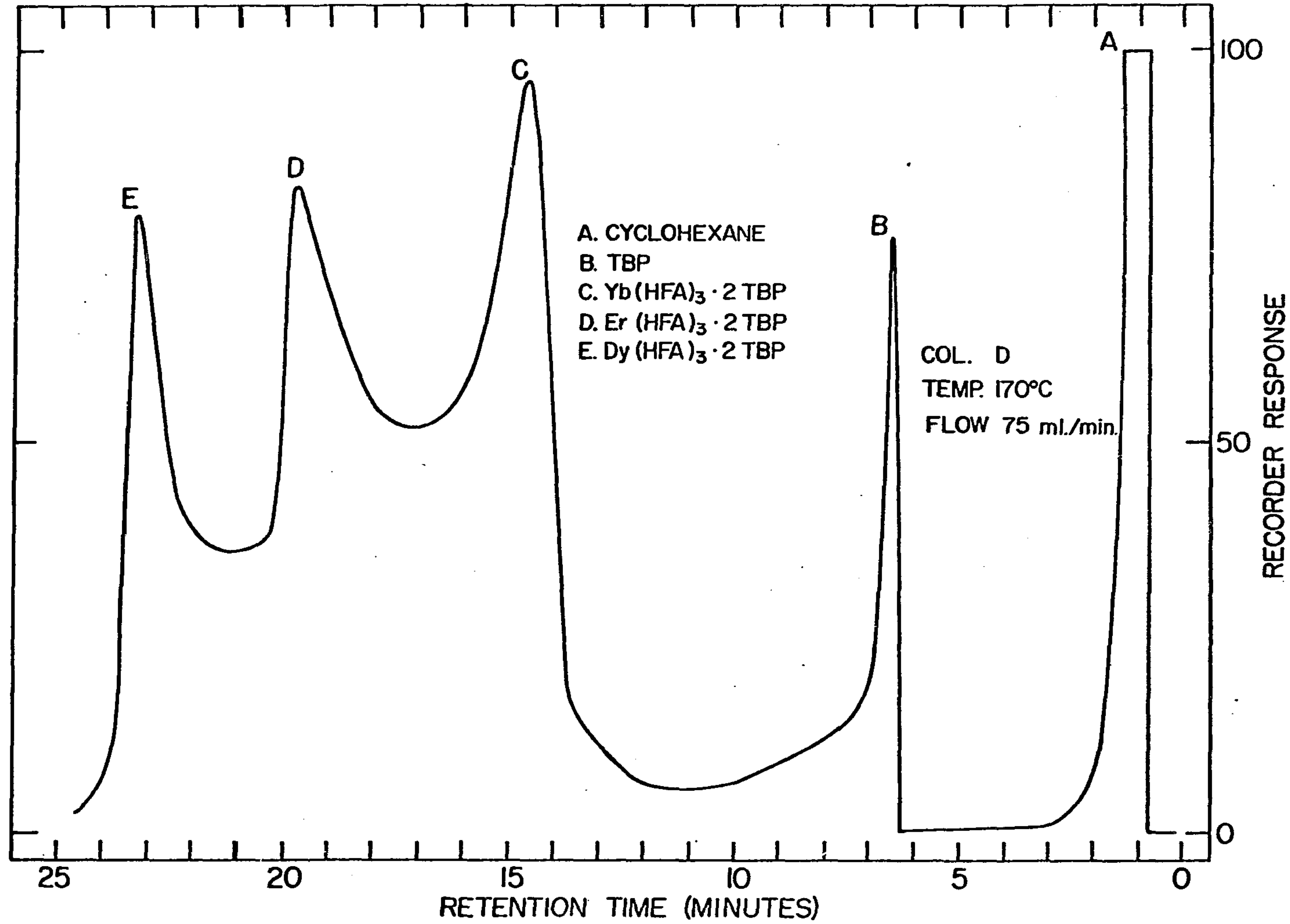


Figure 20. Gas chromatogram of a mixture of the HHFA and TBP mixed-ligand complexes of Yb^{+3}, Er^{+3}, and Dy^{+3}

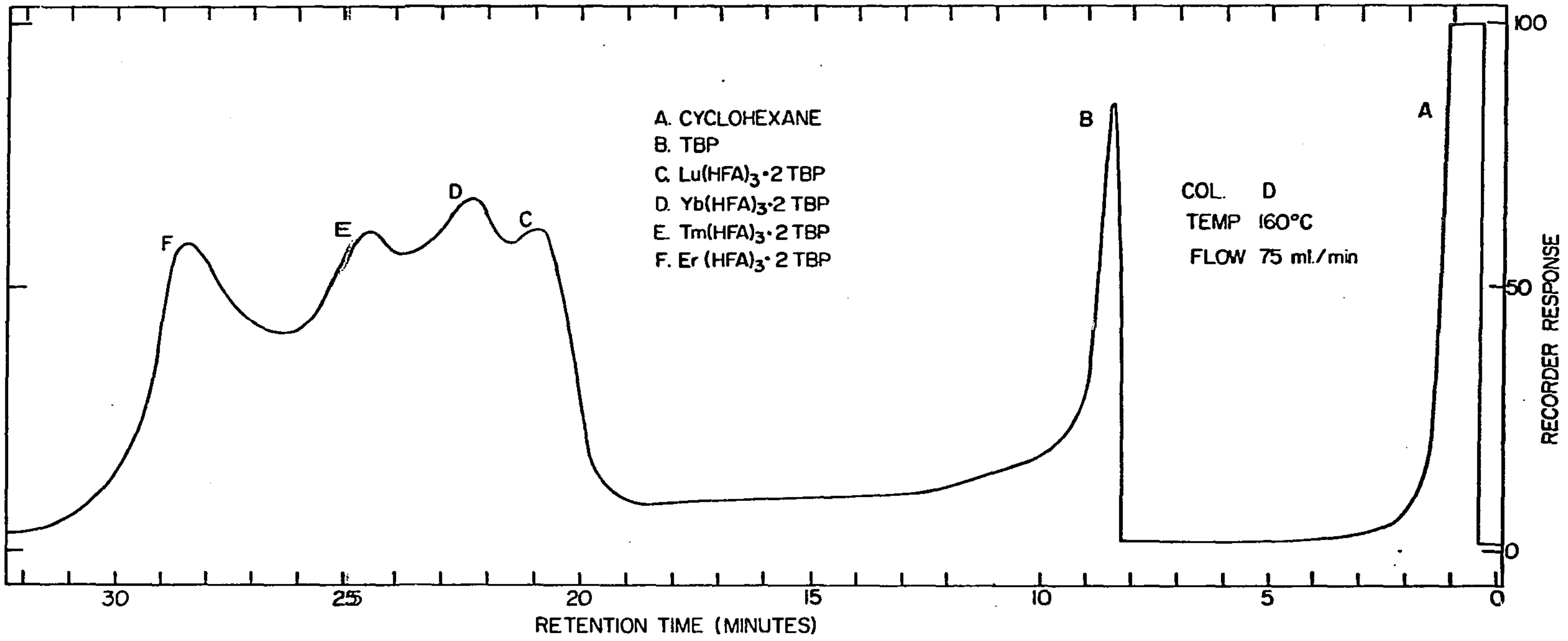


Figure 21. Gas chromatogram of a mixture of the HHFA and TBP mixed-ligand complexes of Lu^{+3}, Yb^{+3}, Tm^{+3}, and Er^{+3}

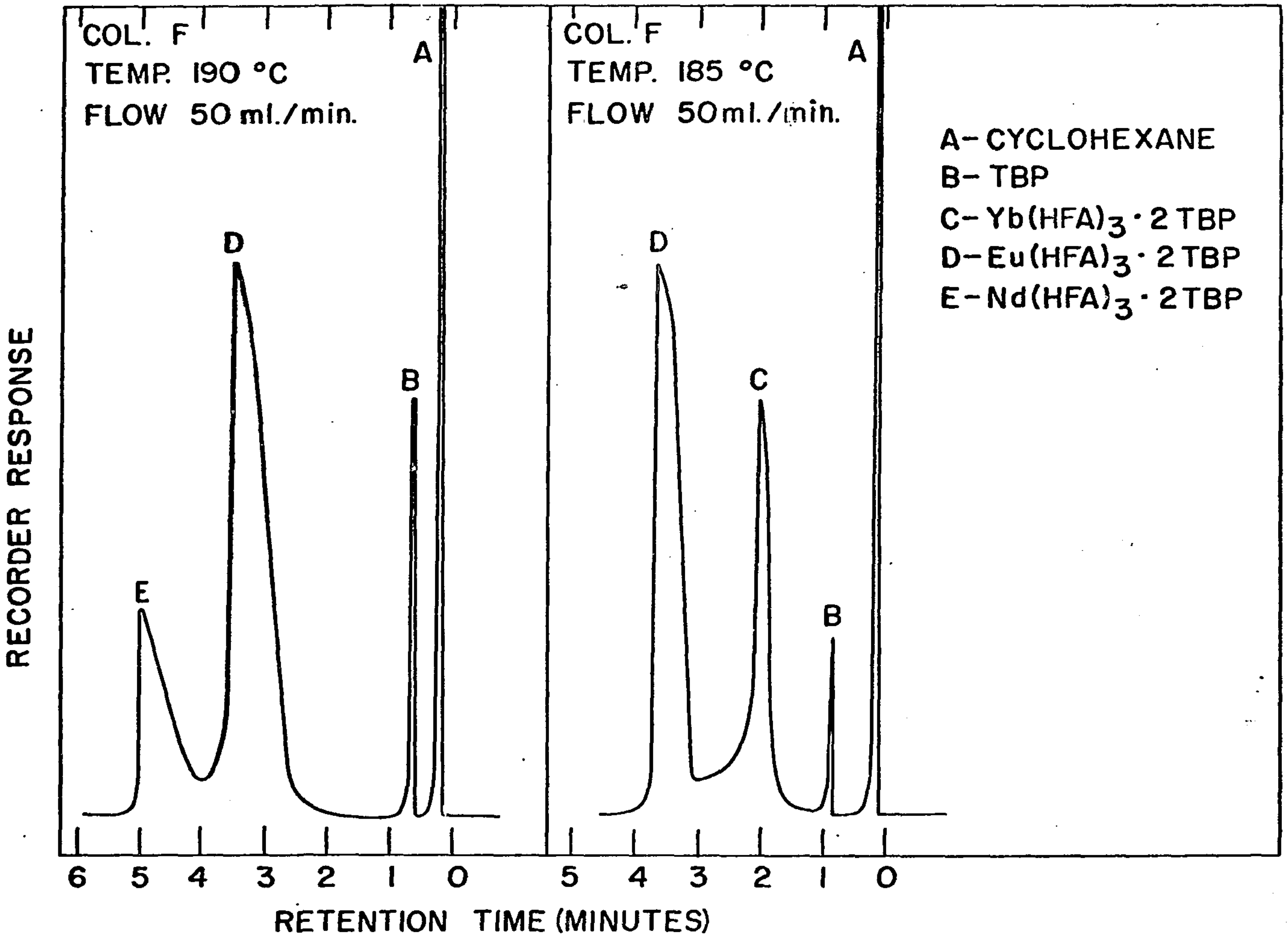


Figure 22. Gas chromatograms of two component mixtures of rare earth complexes of the mixed ligands HHFA and TBP

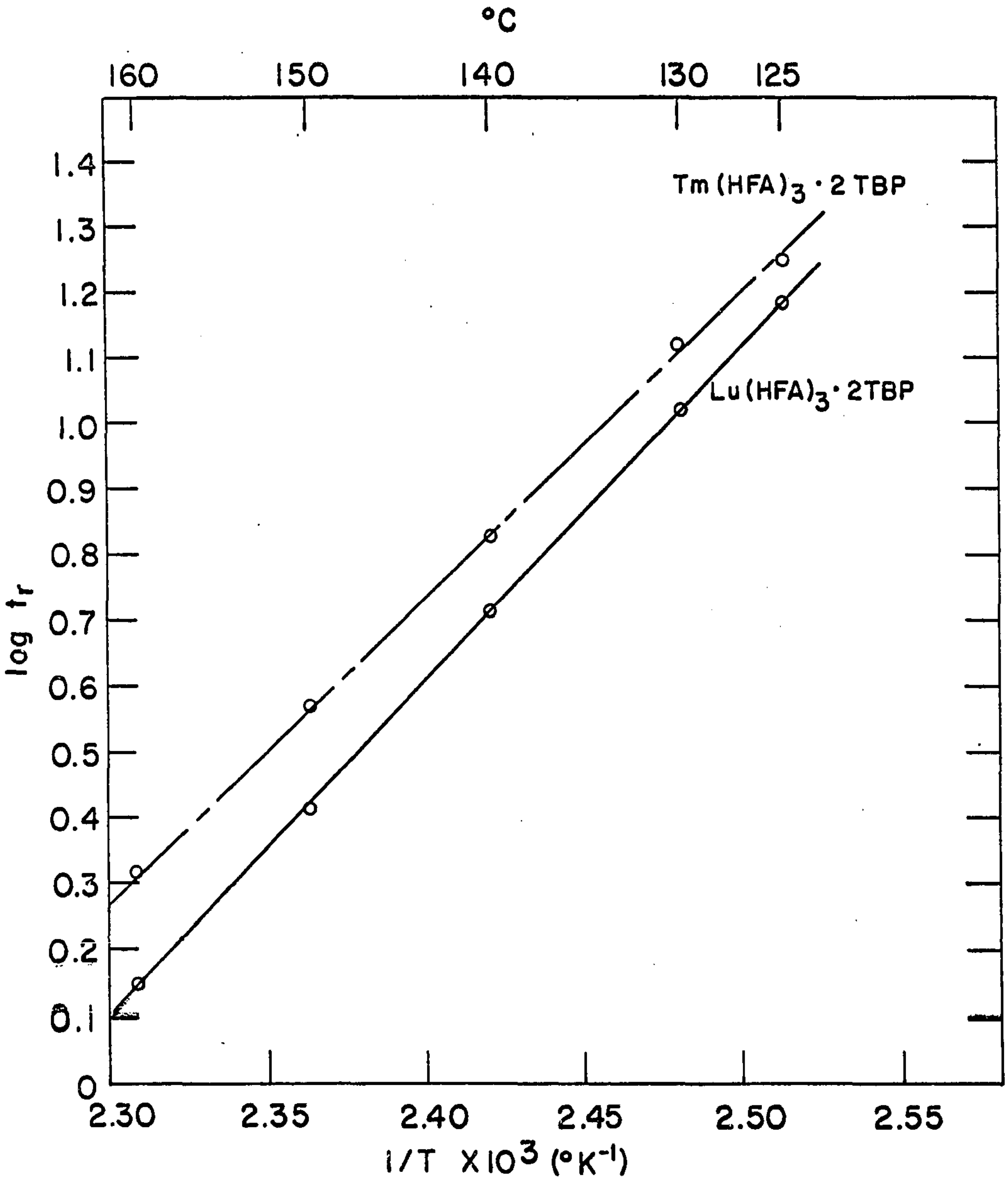


Figure 23. Dependence of the logarithm of the retention time, t_r, on column temperature for Tm(HFA)$_3$·2TBP and Lu(HFA)$_3$·2TBP

plot indicating normal chromatographic behavior and the low temperatures at which the complexes were chromatographed. The lutetium complex, $Lu(HFA)_3 \cdot 2TBP$, which has a formula weight of 1328 was readily chromatographed at 125°C. Lower temperatures are very likely possible with less retentive columns. The importance of lower temperatures is the increased selection of stationary phases that may be used without danger of "bleeding" from the column.

Table 15. Retention time and temperature data for $Lu(HFA)_3 \cdot 2TBP$ and $Tm(HFA)_3 \cdot 2TBP$

Temperature		Retention time (minutes)[a]	
°K	°C	$Lu(HFA)_3 \cdot 2TBP$	$Tm(HFA)_3 \cdot 2TBP$
433	160	1.40	2.10
423	150	2.60	3.72
413	140	5.16	6.80
403	130	10.44	13.18
398	125	15.32	17.79

[a] Obtained with column I at a flow rate of 45 ml/min.

<u>Quantitative studies</u> Figure 24 displays analytical curves for $Eu(HFA)_3 \cdot 2TBP$ and $Tm(HFA)_3 \cdot 2TBP$; the data are given in Table 16. These analytical curves are linear for concentrations greater than approximately 10^{-3} molar. The extrapolation of this portion, however, does not pass through the origin. This deviation is very likely a result of the formation of oxide particles in the flame and on the burner tip and electrodes of the detector.

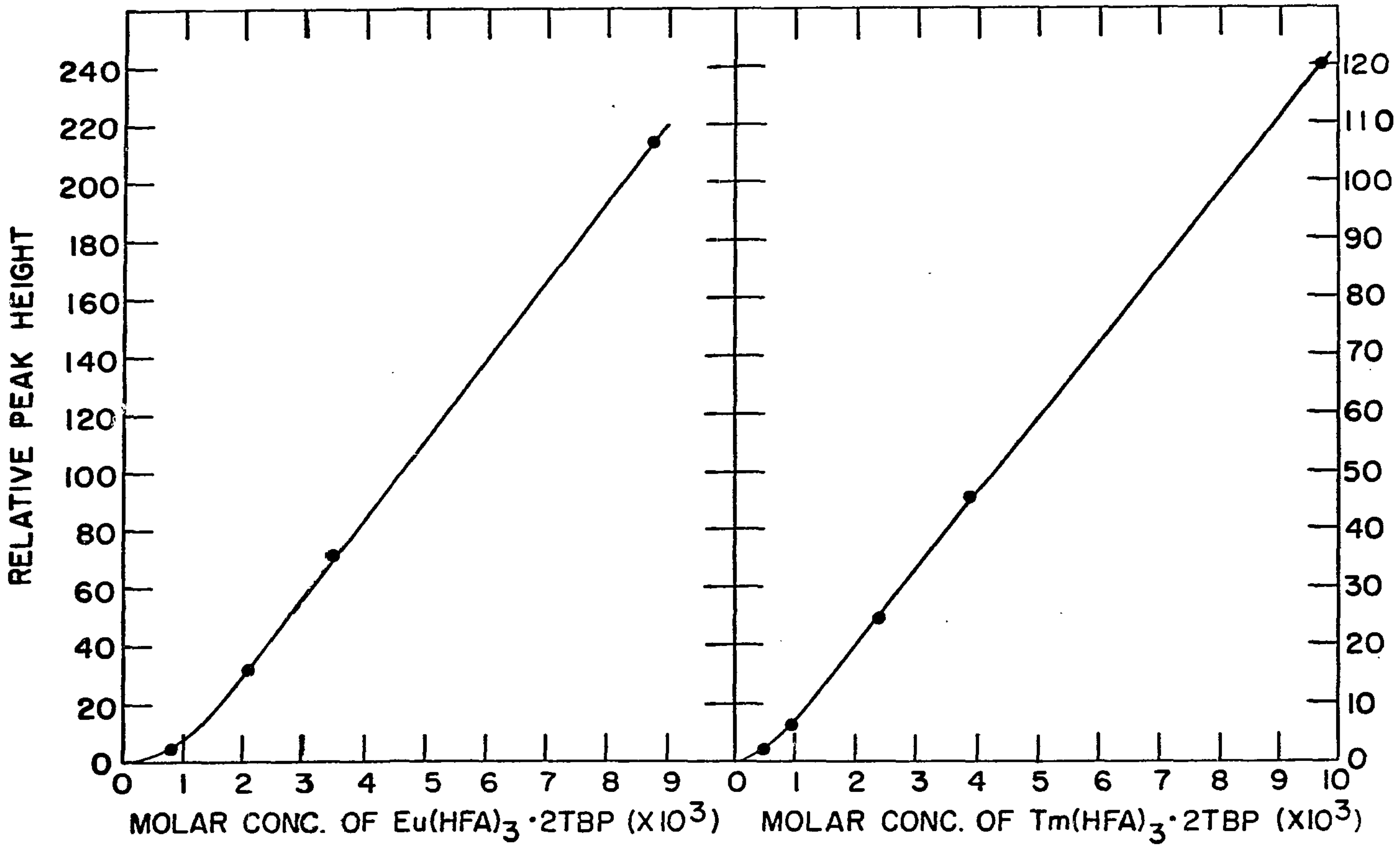


Figure 24. Dependence of relative peak height on the concentration of $Eu(HFA)_3 \cdot 2TBP$ and $Tm(HFA)_3 \cdot 2TBP$

Table 16. Concentration and peak height data from extractions of Tm^{+3} and Eu^{+3} with HHFA and TBP

M	$[M^{+3}]$[a]	Attenuation	Measured peak height[b]	Relative peak height
Tm	$9.7x10^{-3}$	$2x10^4$	60	1200
	$3.9x10^{-3}$	$5x10^3$	91	460
	$2.4x10^{-3}$	$5x10^3$	50	250
	$9.4x10^{-4}$	$2x10^3$	35	70
	$4.7x10^{-4}$	$1x10^3$	25	25
Eu	$8.8x10^{-3}$	$5x10^4$	43	2150
	$3.5x10^{-3}$	$1x10^4$	71	710
	$2.1x10^{-3}$	$5x10^3$	64	320
	$8.2x10^{-4}$	$1x10^3$	50	50

[a] Initial concentration of M^{+3} in aqueous phase.

[b] Obtained with column G at a temperature of 160°C and a flow rate of 45 ml/min.

These data also reveal the response of the flame ionization detector to be greater for the europium complex than for the thulium complex by a factor of about two. Hill and Gesser (35) have shown that the response of the flame ionization detector also varies with the metal for the simple chelates of HHFA.

The samples used in this study were prepared by extraction from a series of dilutions of standardized rare earth chloride solutions. The same stock solutions of HHFA and TBP were used for each extraction. Under these conditions the lowest detectable concentration of the complexes was limited by the excess TBP. Tailing of the chromatographic peak for TBP into the peaks for the complexes restricted quantitative detection to the values shown in Table 16.

Identification of eluted species

Identification of the material eluted from the gas chromatograph was necessary to confirm any conclusions drawn from the chromatograms. The infrared spectral analysis of two fractions of the eluent from an injection of $Pr(HFA)_3 \cdot 2TBP$ has already been mentioned, and the technique for collecting the eluted samples was described in the EXPERIMENTAL PROCEDURES. Conclusive identification of the eluents is discussed in the following sections.

Fluorescence spectrum of europium complex The complex of europium with the mixed ligands HHFA and TBP was chosen for several of the initial studies because it is centrally located in the series of rare earths and because of its fluorescence. This strong red fluorescene was readily visible and permitted easy monitoring of the complex. Confirmation that europium was present in the eluted material was accomplished by comparing the apparent fluorescence spectrum of the cyclohexane phase from an extraction of europium with HHFA and TBP to the spectrum of the eluted sample dissolved in cyclohexane. The two samples possessed the identical spectrum which is shown in Figure 25. The apparent activating wavelength was 348 mμ.

Carbon and hydrogen analysis of europium complex The results of a carbon-hydrogen analysis of a collected sample of eluted $Eu(HFA)_3 \cdot 2TBP$ are shown in Table 17. The agreement of the calculated values and the values found is satisfactory considering the small size of the sample (4.22 milligrams). A combustion technique was employed for this analysis. Carbon was determined as CO_2 adsorbed on Ascarite, and hydrogen was determined as H_2O adsorbed on Anhydrone.

Table 17. Carbon-hydrogen analysis of $Eu(HFA)_3 \cdot 2TBP$ collected from gas chromatograph

Element	Weight % found[a]	Weight % calculated
C	35.18	35.78
H	4.88	4.36

[a] Sample size = 4.22 mg.

Infrared spectral analysis Infrared spectra of HHFA, TBP, hydrated $Ni(HFA)_2$, and the G.C. eluents from the extractions of europium and lutetium with HHFA and TBP were obtained to confirm the presence of TBP in the eluted complexes. The spectra of HHFA and TBP were obtained from neat samples, the solid chelate of nickel was run as a Nujol mull, and the collected eluent samples were dissolved in carbon tetra-

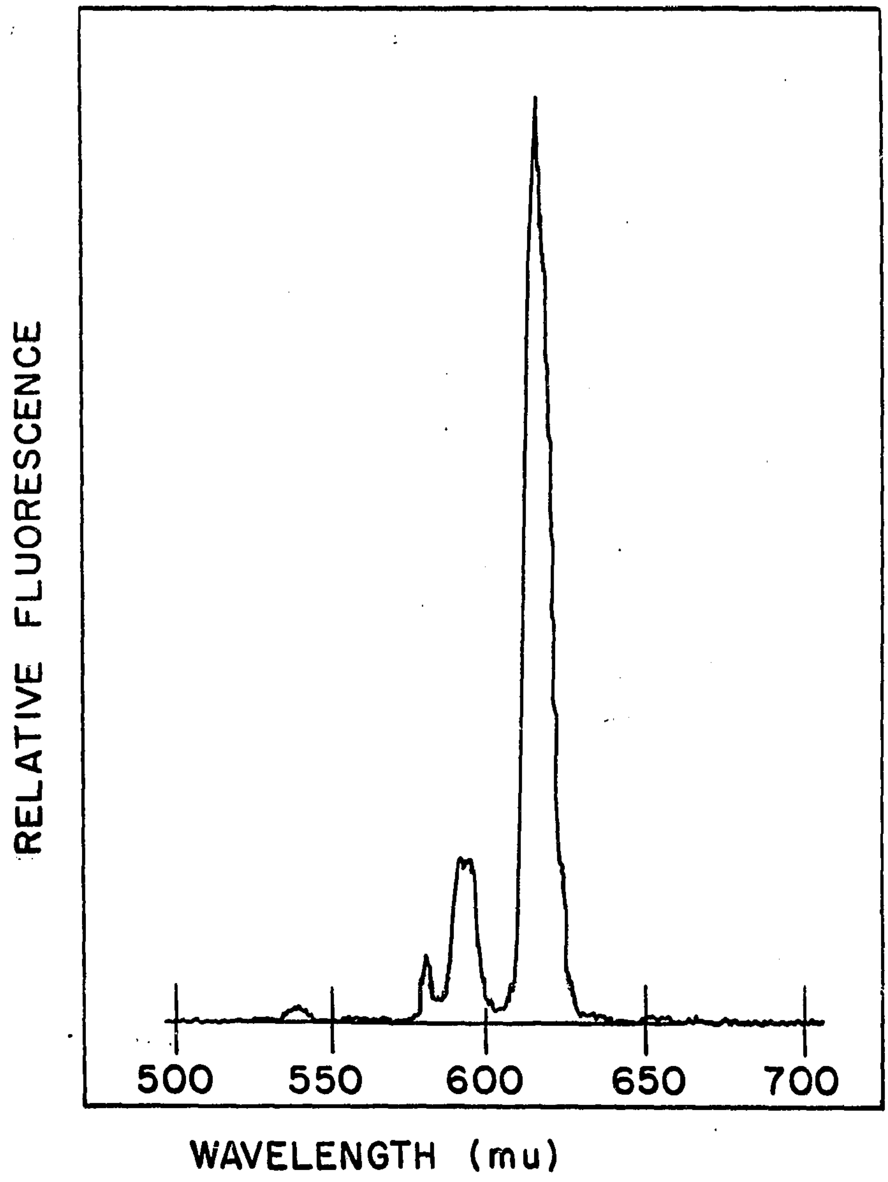


Figure 25. Apparent fluorescence spectrum of Eu(HFA)$_3$·2TBP

chloride for spectral analysis. The infrared spectra of HHFA, TBP, and the two complexes of the rare earths are shown in Figures 26 and 27, and the assignments for the major bands are given in Table 18.

The assignments for the bands in the spectrum of HHFA and those attributed to HFA in the spectra of the complexes agree with reported assignments (3,49,51,54,87), with the exception of the $C\overset{\cdots}{-}O$ and $C\overset{\cdots}{-}C$ stretching frequencies in the region 1500 to 1660 cm^{-1}. Lawson (43) has summarized the work of several investigators who have empirically assigned the higher frequency bands in this region to the $C\overset{\cdots}{-}O$ stretch and the lower frequencies to the $C\overset{\cdots}{-}C$ stretch. Nakamoto (54) has calculated by normal coordinate analysis that these assignments should be reversed. Because of this discrepancy, the bands in this region are grouped in Table 18 and no definite assignments given.

The presence of the C-H and [P-O]-R stretching frequencies in the spectra of the complexes of the rare earths confirms the presence of TBP in these eluted samples. The assignments for the P=O and [P-O]-R bands agree with those reported by Bellamy (4).

Ferraro <u>et</u> <u>al</u>. (29) reported the [P→O]-M band for $Eu(NO_3)_3 \cdot 3TBP$ to be at 1212 cm^{-1} and for $Lu(NO_3)_3 \cdot 3TBP$ to occur at 1220 cm^{-1}. Referring to the spectra in Figure 27, it appears that these bands overlap the C-F stretching

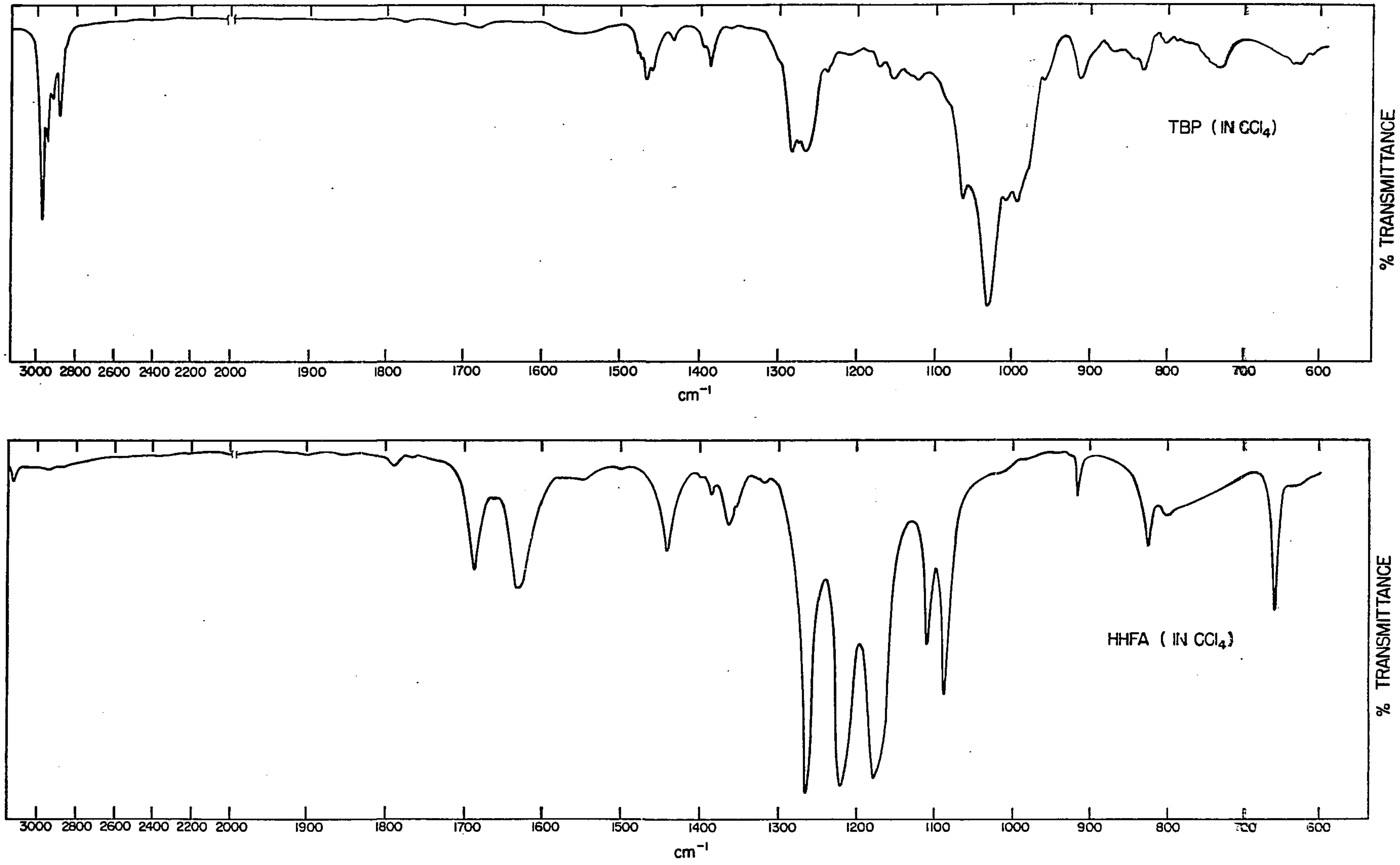


Figure 26. Infrared spectra of HHFA and TBP

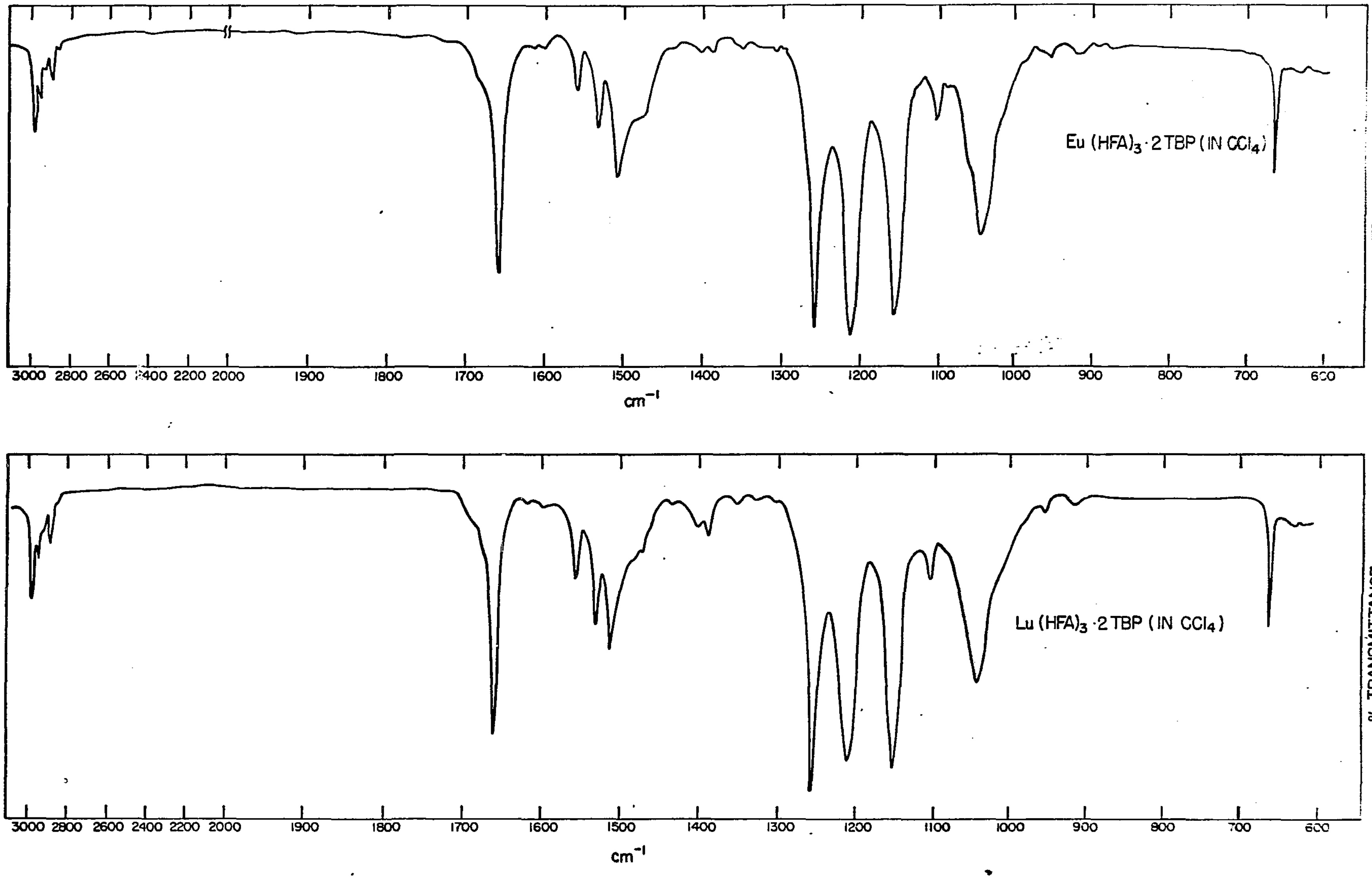


Figure 27. Infrared spectra of Eu(HFA)$_3$·2TBP and LU(HFA)$_3$·2TBP

Table 18. Assignment of infrared spectral bands (cm^{-1}) for HHFA, TBP, hydrated Ni(HFA)$_2$, and the collected G.C. effluents of the Eu^{+3} and Lu^{+3} extractions with HHFA and TBP

Assignment	HHFA[a]	TBP	Ni(HFA)$_2$[b] hydrate	Eu HFA-TBP[c]	Lu HFA-TBP[c]
H_2O			3472		
OH str.	3126				
CH str.		2968		2976	2976
		2938		2946	2958
		2910		2922	2924
		2878		2886	2886
C=O str.	1688				
C=C str.	1632				
C$\overset{\cdots}{-}$C and			1650	1657	1660
C$\overset{\cdots}{-}$O str.			1615	1556	1555
			1565	1530	1529
			1539	1506	1510
OH bend	1442				
CH bend		1469		1482	1480
		1385		1395	1392
C-O str.	1367				
P=O str.		1282			
		1263			
CF str.	1264		1263	1255	1256
	1220		1225	1210	1210
	1176		1150	1154	1152
	1109		1096	1100	1102
	1086				
[P-O]-R str.		1027		1040	1038
	916		908	--[d]	--[d]
	657		675	662	660

[a] HHFA is primarily in the enol form (APPENDIX A).

[b] Nujol mull.

[c] CCl_4 solvent.

[d] Blanked out by CCl_4 solvent.

frequency at 1210 cm^{-1}. This would explain the broader and less intense band at 1210 cm^{-1} for $Lu(HFA)_3 \cdot 2TBP$ compared to that for $Eu(HFA)_3 \cdot 2TBP$.

A quantitative infrared spectral determination of the ratio of HFA to TBP was performed on a collected sample of the eluted europium complex. Solutions of known concentrations of TBP and HHFA in carbon tetrachloride were used as the standards, and a comparison of the C-H stretching frequency at 2976 cm^{-1} (representing the TBP) and the C-F stretching frequency at 1255 cm^{-1} (HHFA) was used for the determination. The value for the ratio of HHFA to TBP calculated from four samples was 1.4 ± 0.2; this agrees with the desired value of 1.5 for complexes of the form $M(HFA)_3 \cdot 2TBP$.

Identification of extracted species

The general form of the eluted complexes of the rare earths being $M(HFA)_3 \cdot 2TBP$ agrees with the stoichiometry reported by Sekine and Dryssen (72) for the complexes of the rare earths formed by extraction with the mixed ligands HTTA and TBP. The assumption that the metal to HFA ratio was also 1:3 in the extracted species was considered justified on the basis of the work of other investigators (34,73,74) who have shown that the rare earth species extracted by other β-diketones and monofunctional neutral donors (S) have the composition $M(\beta\text{-diketone})_3 \cdot 2S$ or $M(\beta\text{-diketone})_3 \cdot S$. It was considered necessary, however, to verify the TBP content of the extracted complexes. This was accomplished with a solvent extraction-molar ratio study similar to that employed by Carey (15, p. 103).

This type of study is based on the fact that the trivalent rare earths are very poorly extracted by HHFA alone. The concentration of the simple chelate of the rare earth and HHFA is small compared to the concentration of the mixed-ligand complex, and it contributes only slightly to the amount of rare earth extracted.

The formation of the mixed-ligand complex is represented by the reaction

$$M^{+3} + 3HHFA + nTBP \rightleftharpoons M(HFA)_3 \cdot nTBP + 3H^+.$$

When the initial concentration of the HHFA is kept constant and in excess and the concentration of H^+ is placed at a low level (pH = 5.5) shifting the equilibrium to the right, the amount of TBP becomes the limiting quantity in the extraction. One hundred per cent extraction will, therefore, occur when the stoichiometric amount of TBP has been added. The extraction of the rare earths was monitored by two methods: 1) complexometric titration of the aqueous phase and 2) gas chromatographic analysis of the organic phase. Procedural details are given in the section EXPERIMENTAL PROCEDURES.

Figure 28 shows the percentage of europium extracted from the aqueous phase as a function of the mole ratio of the concentration of TBP to the original concentration of europium in the aqueous phase. The data for this curve are given in

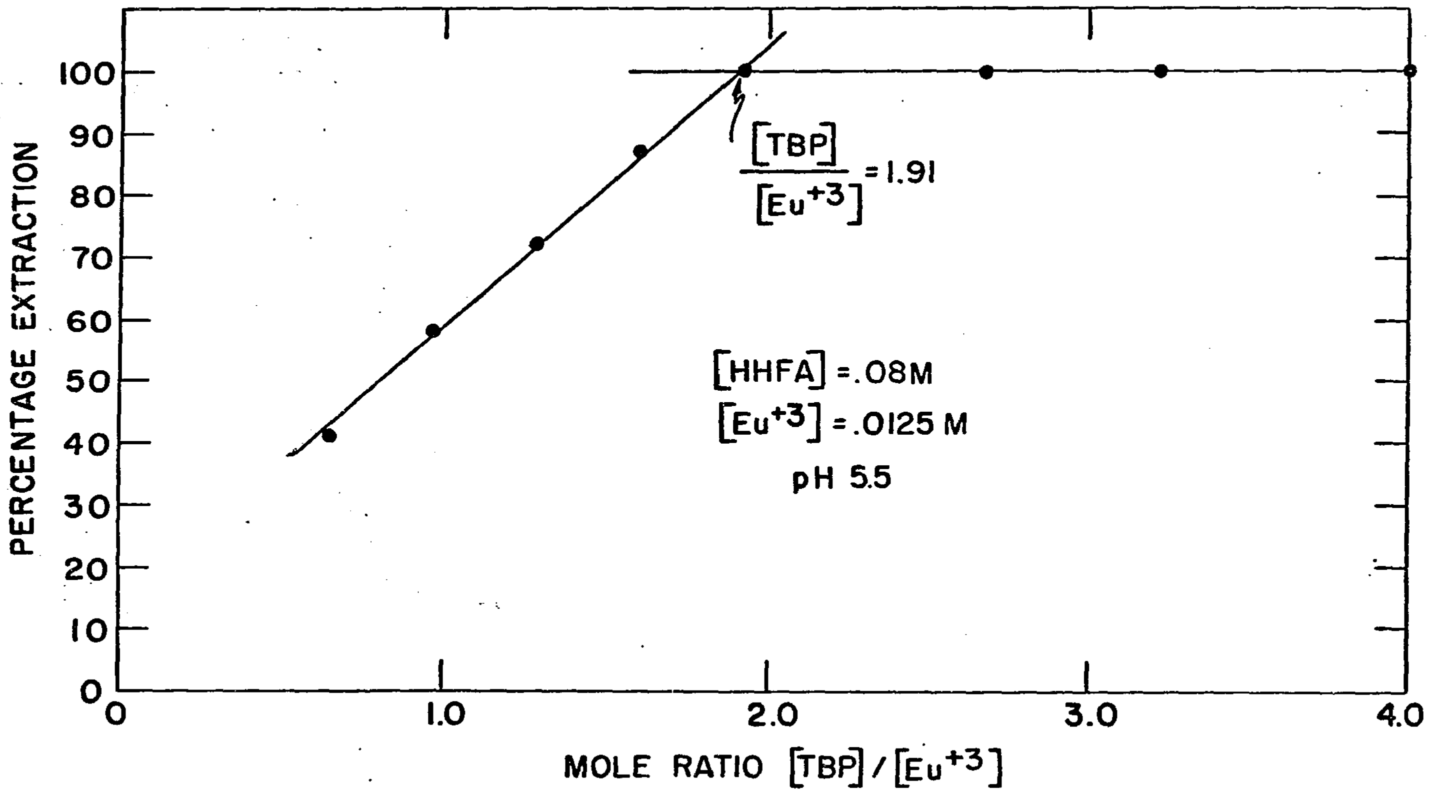


Figure 28. Dependence of the amount of Eu(III) extracted in the presence of excess HHFA on the ratio of the concentration of TBP to the original concentration of europium in the aqueous phase

Table 19. This system exhibited 100% extraction at a molar ratio of approximately 2:1 as anticipated. Data points for molar ratios of less than 0.5:1 could not be obtained because of the formation of a precipitate. This precipitate was probably the sodium salt of the $Eu(HFA)_4^+$ complex.

Table 19. Dependence of % extraction of Eu^{+3} on the ratio of $[TBP]_o$ to $[Eu^{+3}]$

$[TBP]_o$[a]	$\frac{[TBP]_o}{[Eu^{+3}]}$	% Extraction
0.0534	4.27	100
0.0401	3.22	100
0.0334	2.67	100
0.0240	1.92	100
0.0200	1.60	87
0.0160	1.28	72
0.0120	0.96	58
0.0080	0.64	41
0.0040	0.32	--[b]
0.0013	0.16	--[b]

Conditions[a]: $[HHFA]_o = 0.08$ M

$[Eu^{+3}] = 0.0125$ M

pH = 5.5

[a] Initial concentrations.

[b] Precipitate formation occurs.

The HTTA complex of lutetium is reported to form a weaker 2:1 adduct with TBP than does that of europium (72). Figure 29 illustrates the molar ratio study for the extraction of lutetium with HHFA and TBP confirming that the 2:1 adduct was

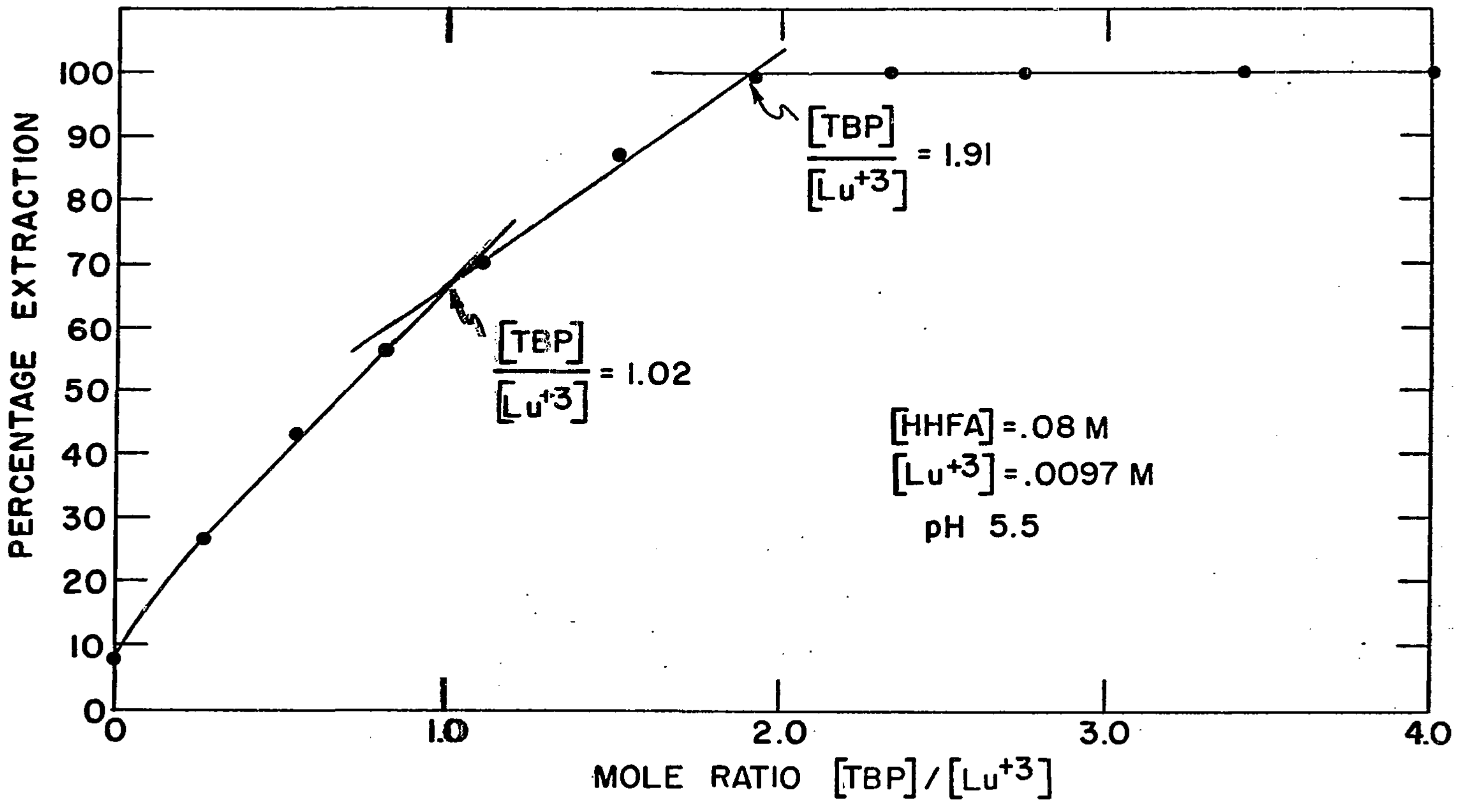


Figure 29. Dependence of the amount of Lu(III) extracted in the presence of excess HHFA on the ratio of the concentration of TBP to the original concentration of lutetium in the aqueous phase

the extracted species, although formation of a 1:1 adduct also appeared to occur at lower concentrations of TBP. No precipitate formation occurred with the lutetium system, apparently because the smaller lutetium ion sterically hinders formation of a tetrakis complex.

Figure 30 shows the relationship between the relative peak height of the gas chromatographic peak for $Lu(HFA)_3 \cdot 2TBP$ versus the TBP/lutetium molar ratio for the system just discussed. This plot also indicates the formation of 2:1 and 1:1 adducts. The data for these studies of the lutetium are given in Table 20.

Table 20. Dependence of % extraction of Lu^{+3} and relative peak height on the ratio of $[TBP]_o$ to $[Lu^{+3}]$

$[TBP]_o$[a]	$\frac{[TBP]_o}{[Lu^{+3}]}$	% Extraction	Measured peak height	Relative peak height
0.0399	4.11	100	71	100
0.0331	3.41	100		
0.0266	2.74	100	70	99
0.0226	2.33	100		
0.0186	1.92	99.7	69	98
0.0146	1.51	86.7	58	82
0.0107	1.10	70.0	48	68
0.0080	0.82	56.3	37	52
0.0053	0.55	43.1	23	33
0.0026	0.27	26.6	8	12
0.0	0.0	8.0	0	0

Extraction conditions[a]:
$[HHFA]_o = 0.08M$
$[Lu^{+3}] = 0.0097\ M$
pH = 5.5

G.C. conditions:
Col. G
Temp. 170°C
Flow 60 ml/min

---

[a] Initial concentrations.

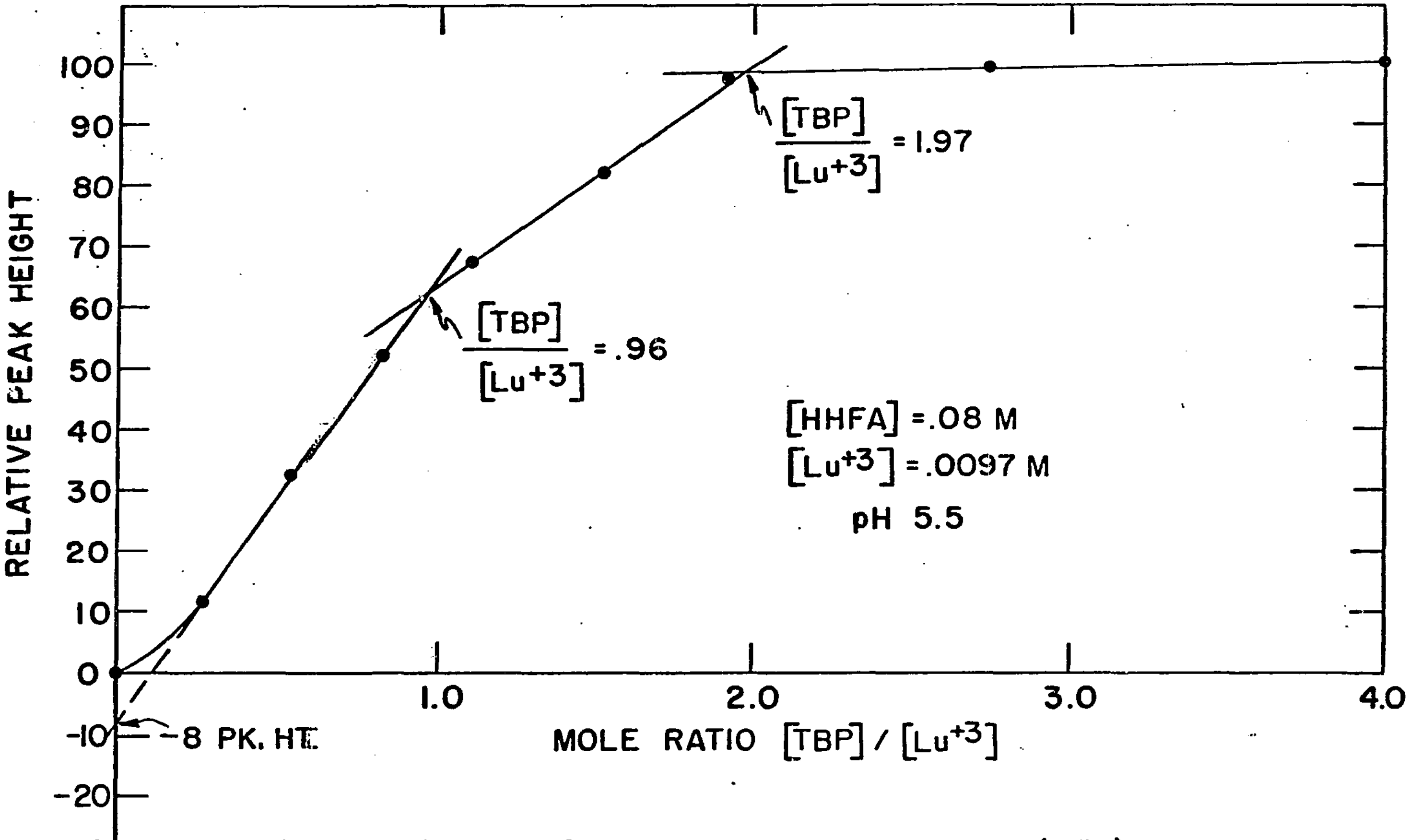


Figure 30. Dependence of the relative peak height for $Lu(HFA)_3 \cdot 2TBP$ from the organic phase of an extraction with HHFA and TBP on the ratio of the concentration of TBP to the original concentration of lutetium in the aqueous phase

The negative peak height intercept of the extrapolation of the linear portion of Figure 30 agrees with the amount of lutetium extracted by HHFA in the absence of an adduct as represented by the intercept in Figure 29. The species formed between the lutetium and HHFA at zero concentration of TBP and extracted into the organic phase did not contribute to the chromatographic peak being measured, and it apparently did not chromatograph at all because no other extraneous peaks were present in the chromatogram.

Dependence of extraction on pH and time

The extractions discussed to this point were performed from an aqueous solution buffered to pH 5.5 with an acetate buffer. The following study was undertaken to determine at how low a pH extraction of the rare earths could be accomplished with HHFA and TBP.

As in the preceding extraction studies, the aqueous phase was analyzed by titration with EDTA and the organic phase by gas chromatography. The results are shown in Table 21 and Figures 31 and 32. The pH values in the figures are the values measured at equilibrium. Although the curves are slightly different for the two phases, both show 50% extraction at approximately pH 0.7 and 100% extraction for pH values greater than two. Relative peak heights were used for the gas chromatographic study, and it is assumed that the maximum relative peak height represents 100% extraction. The

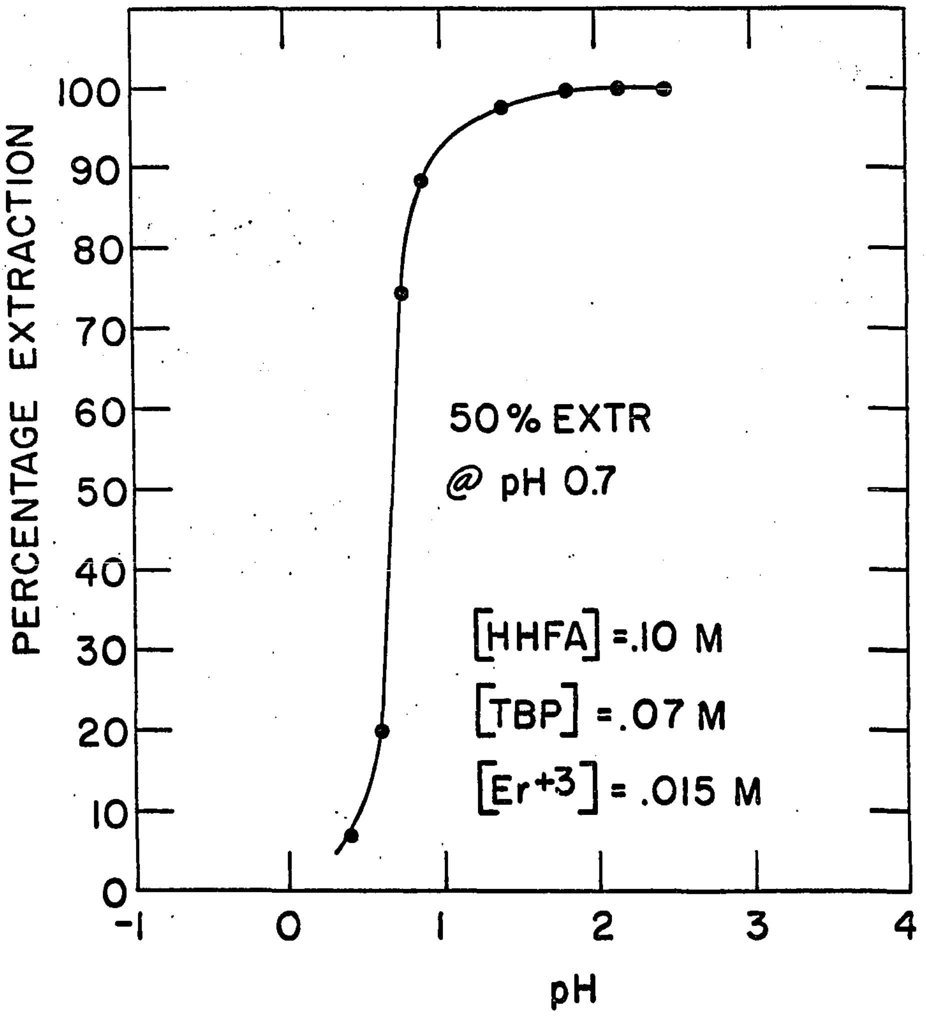


Figure 31. Dependence of the amount of Er(III) extracted on the equilibrium pH of the aqueous phase

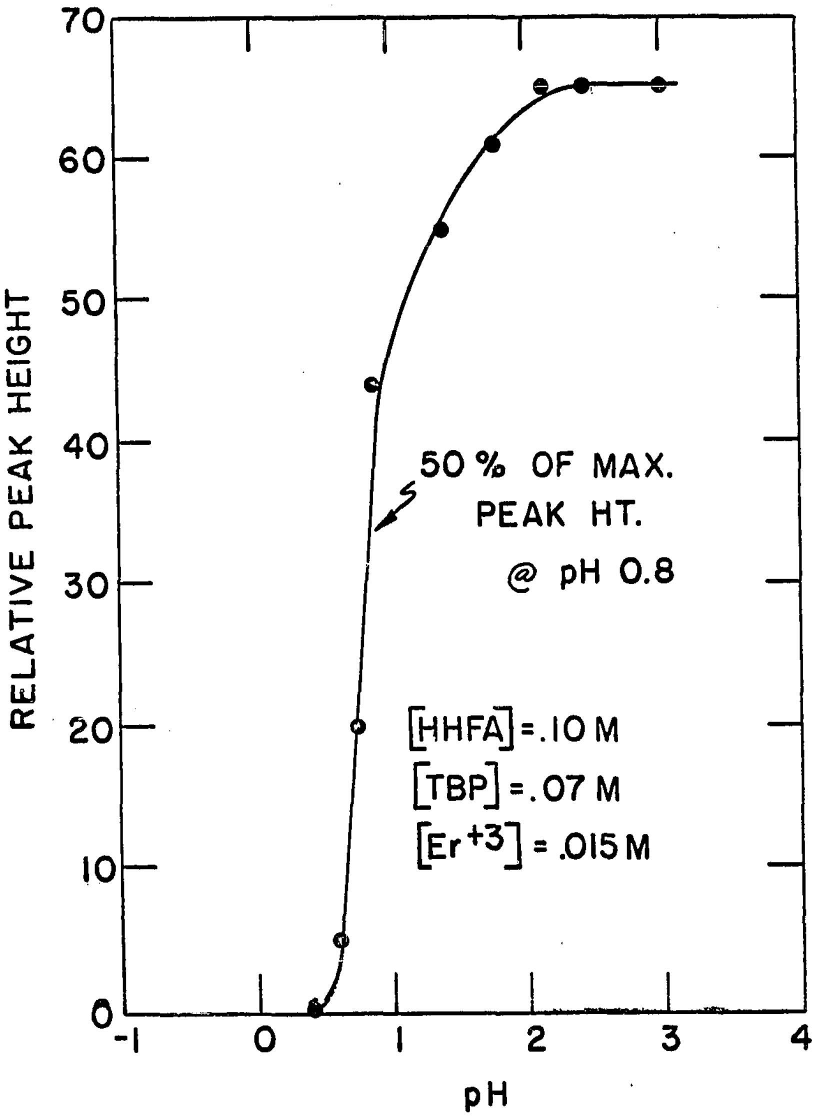


Figure 32. Dependence of the relative peak height for $Er(HFA)_3 \cdot 2TBP$ on the equilibrium pH of the aqueous phase

slight difference in the two curves might be attributed to the lower accuracy of the G.C. analysis as compared to the complexometric titration, or it may be a result of the extraction of some species other than $Er(HFA)_3 \cdot 2TBP$ from the more acidic solutions.

Table 21. Dependence of % extraction of Er^{+3} and peak height on pH

Equilibrium pH	% Extraction	Peak height
2.45	100	65
2.15	100	65
1.80	99.5	61
1.40	97.5	55
0.88	88.6	44
0.75	74.6	20
0.60	20	5
0.40	7	1

Extraction conditions[a]:		G.C. conditions:	
$[HHFA]_o$	= 0.10 M	Col.	G
$[TBP]_o$	= 0.07 M	Temp.	170°C
$[Er^{+3}]$	= 0.015 M	Flow	60 ml/min

[a] Initial concentrations.

A similar study was made of the percentage extraction and relative peak height as a function of the time the sample was agitated prior to sampling. Maximum peak heights and 100% extraction were obtained for equilibration times of 15 minutes, eight hours, and 24 hours.

Interference by other metals

Comparative gas chromatograms were obtained for samples from the cyclohexane phase of HHFA and TBP mixed-ligand extractions of some trivalent rare earths and of several other cations. These chromatograms indicated that several other metals will interfere in the analysis of the rare earths by the extraction and gas chromatography of their mixed-ligand complexes of HHFA and TBP.

Zinc and uranium (as uranyl), both well documented as forming mixed complexes with HTTA and TBP, formed extractable species with HHFA and TBP giving broad and distorted chromatographic peaks interfering severely with all but the four or five least volatile rare earth complexes. Thorium, which Healy (33) has reported forming a complex of the form $Th(TTA)_4 \cdot TBP$, produced a chromatogram with an extremely broad peak interfering with the determination of all of the rare earths. These extracted species of zinc, uranium, and thorium had detector sensitivities similar to those of the complexes of the rare earths and are expected to be serious interferences in concentrations approximately equal to the rare earth concentration.

Scandium appeared to be partially extracted, producing a broad chromatographic peak which would be a serious interference at scandium concentrations five to ten times that of the rare earths in the same solution. Sekine and Dyrssen

(71) have reported the extraction of $Sc(TTA)_3 \cdot TBP$ where the bonding of the TBP is relatively weak compared to the bonding of the adduct in the HTTA and TBP mixed ligand complexes of the rare earths. Aluminum, which would not be expected to form a mixed complex, did not form a chromatographable species and would not interfere.

Conclusions

The mixed-ligand system HHFA and TBP shows definite promise as a gas chromatographic reagent for the rare earths. The complexes of the rare earths with these mixed ligands are generally sufficiently volatile to permit suitable variation of operating conditions to effect analytical separations and determinations of the rare earths.

The principal difficulty in chromatographing the complexes is the partial thermal decomposition of the less volatile complexes, namely those of lanthanum, cerium, praseodymium, neodymium, and perhaps samarium. Semiquantitative analyses of these rare earths, however, should still be possible even if partial decomposition cannot be avoided.

The preparation of the chromatographable species by solvent extraction is the primary advantage of this system over the β-diketones, HPIV and HFOD, the rare earth chelates of which have been gas chromatographed by other workers.

Rapid and complete extraction of the rare earths even at low pH values makes HHFA and TBP a practical extraction system. The prime disadvantage of this extraction system is that it extracts other ions, in addition to those of the rare earths, that form mixed-ligand complexes. These other complexes interfere in the gas chromatographic determination of the rare earths; therefore, mixtures of rare earths with some other metals will require an initial separation before the rare earths can be analyzed by gas chromatography of their mixed-ligand complexes of HHFA and TBP.

SUMMARY

Several metal chelates of HTTA and HBTA can be gas chromatographed. The chelates of HBTA are significantly more volatile than those of HTTA and can be chromatographed at lower temperatures, thereby avoiding the thermal decomposition that occurs with some of the HTTA chelates. The use of lightly loaded columns is necessary to minimize the operating temperature of the column oven and reduce decomposition of the chelates. These columns although relatively inefficient are capable of effecting separations of several different metal chelates of HBTA. Confirmation that the eluted species and the original chelates were the same was accomplished by comparison of their ultraviolet spectra.

A study of the chromium chelate of HBTA indicates that $Cr(BTA)_3$ can be chromatographed at least over the temperature range 170 to 230°C and in concentrations from 6×10^{-4} to 4×10^{-2} molar. A partial resolution of the geometrical isomers of $Cr(BTA)_3$ is apparently possible by gas chromatography.

All of the chelates chromatographed are anhydrous when prepared from an aqueous solution of the metal salt. Hydrated chelates are insufficiently soluble in an organic solvent for gas chromatographic study or preparation by solvent extraction.

The two ligands, HBTA and HTTA, have very similar extraction properties; therefore, the greater volatility of the HBTA complexes renders it more worthy of additional study. However, high operating temperatures are still required for the HBTA chelates, and further investigation of the application of gas chromatography to the chelates of HBTA is not considered warrented except for those metals which cannot be extracted by ligands, such as HTFA, forming more volatile chelates.

On the other hand the mixed ligands HHFA and TBP show excellent potential as a gas chromatographic reagent for the rare earths. Gas chromatograms are obtainable for the HHFA and TBP mixed-ligand complexes of all the rare earths with partial decomposition occurring only in the case of the four or five least volatile complexes. Unique retention times are obtained for the complexes of the rare earths, and many separations are possible including partial resolution of the complexes of rare earths situated consecutively in the lanthanide series. The most volatile complexes can be chromatographed at temperatures as low as 125°C. Volatility increases with a decrease in the radius of the trivalent rare earth.

The species extracted from aqueous solutions of the rare earth chlorides by HHFA and TBP and those collected in the effluent from the gas chromatograph are analyzed as being of the form $M(HFA)_3 \cdot 2TBP$. One hundred per cent extraction of the rare earth from an aqueous solution can be accomplished with equilibration times of less than 15 minutes and at pH values lower than two. This extraction system also extracts other cations which interfere with the gas chromatographic analysis of the rare earths and will require prior separation.

SUGGESTIONS FOR FUTURE WORK

As mentioned in the preceding SUMMARY, the investigation of the application of gas chromatography to the metal chelates of HTTA and HBTA is not considered to be a particularly worthwhile field for additional study. Additional gas chromatographic work should be done only with those metals for which HBTA can be shown to be a much superior extractant to those ligands forming more volatile chelates.

A stated purpose of this work was to determine the feasibility of using the mixed ligands HHFA and TBP as a gas chromatographic reagent for the rare earths, and it was concluded that the chromatographic and extraction properties of this system were satisfactory for such an application. The following suggestions for future work in this area, therefore, involve an expansion of the chromatographic and extraction studies discussed in this thesis.

Although similar to several ligand pairs discussed in the literature, the mixed ligands HHFA and TBP require further study as an extractant. Such a study should consider the rare earths as well as metals frequently occurring with the rare earths. As was shown, other metals interfere in the gas chromatographic analysis of the rare earth complexes of HHFA and TBP, and preliminary separation is necessary. This separation might be accomplished by varying the extraction conditions, particularly pH. Other factors to consider are the effect of excess reagents and the nature and concentration of the anions in the aqueous phase.

The principal areas of investigation in a continued G.C. study would be improved separations, quantitative applications, and the effect of the extraction conditions on the chromatograms. Extraction conditions have already been shown to be important; tailing of the chromatographic peak for TBP affects the detection limits for the complexes of the rare earths. Metwally et al. (47) have shown that less volatile solvents improve the quantitative results obtained when chromatographing high-boiling compounds.

A study of the quantitative applications would involve a study of detectors and detector responses. The response of the flame ionization detector was shown to vary with the rare earth in the mixed-ligand complex. The electron capture detector is significantly more sensitive to chelates of fluorinated β-diketones than the flame ionization detector (61,63). Phosphorus detectors (12,13,39,46) would be expected to respond well to the mixed-ligand complexes, although they might aggravate the problem of interference by excess TBP. The flame photometric detector (37) is another possibility.

The area in which the most work can be done is that of improving separation. The relatively low operating temperatures required to chromatograph the complexes of the rare earths with the mixed ligands HHFA and TBP should permit the use of a variety of stationary phases without danger of column "bleeding". Open tubular columns may also be usable.

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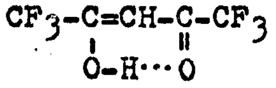
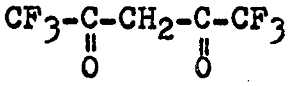
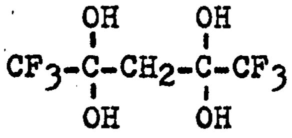
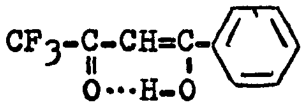
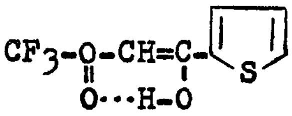
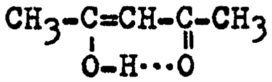
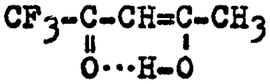
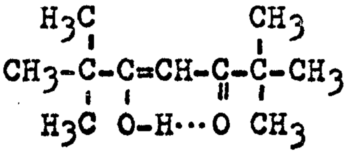
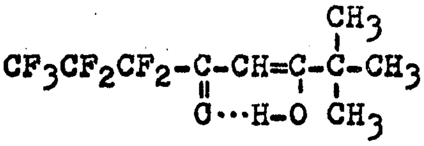
APPENDIX A

Structure and Nomenclature of Ligands

1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone)	HHFA	 $\mathrm{CF_3-\underset{\overset{\mid}{O}-H\cdots}{C}=CH-\underset{\overset{\|}{O}}{C}-CF_3}$ enol form  $\mathrm{CF_3-\underset{\overset{\|}{O}}{C}-CH_2-\underset{\overset{\|}{O}}{C}-CF_3}$ keto form  $\mathrm{CF_3-\overset{OH}{\underset{OH}{C}}-CH_2-\overset{OH}{\underset{OH}{C}}-CF_3}$ dihydrate
4,4,4-trifluoro-1-phenyl-1,3-butanedione (benzoyltrifluoroacetone)	HBTA	
4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyltrifluoroacetone)	HTTA	
2,4-pentanedione (acetylacetone)	HACAC	 $\mathrm{CH_3-\underset{\overset{\mid}{O}-H\cdots}{C}=CH-\underset{\overset{\|}{O}}{C}-CH_3}$
1,1,1-trifluoro-2,4-pentanedione (trifluoracetylacetone)	HTFA	 $\mathrm{CF_3-\underset{\overset{\|}{O}\cdots H-}{C}-CH=\underset{\overset{\mid}{O}}{C}-CH_3}$

2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane)	HPIV	 $CH_3-\overset{H_3C}{\underset{H_3C}{C}}-\underset{O-H\cdots O}{C=CH-C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$
1,1,1,2,2,3,4-heptafluoro-7,7-dimethyl-4,6-octanedione	HFOD	 $CF_3CF_2CF_2-\underset{O\cdots H-O}{C-CH=C}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$
tri-n-butylphosphate	TBP	$(C_4H_7O)_3-P\rightarrow O$
tri-n-butylphosphine oxide	TBPO	$(C_4H_7)_3-P\rightarrow O$

APPENDIX B

Gas Chromatographic Columns

A. 4' x 0.25" o.d., 5% SE-30/DMCS-Chromosorb W (glass)

B. 3' x 0.12" o.d., 5% SE-30/DMCS-Chromosorb W (glass)

C. 4' x 0.25" o.d., 0.5% SE-30/glass beads (glass)

D. 10' x 0.12" o.d., 2% SE-30/DMCS-Chromosorb G (stainless steel)

E. 6' x 0.12" o.d., 10% SE-30/DMCS-Chromosorb W (glass)

F. 1.5' x 0.12" o.d., 0.5% SE-52/glass beads (glass)

G. 4' x 0.12" o.d., 2% SE-30/DMCS-Chromosorb G (glass)

H. 4' x 0.12" o.d., 0.1% SE-30/glass beads (glass)

I. 1' x 0.12" o.d., 10% SE-30/DMCS-Chromosorb W (glass)

J. 4' x 0.25" o.d., 0.5% SE-30/glass beads (copper)

K. 4' x 0.25" o.d., 0.5% SE-30/glass beads (stainless steel)

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