

# Separation and Estimation of Lanthanides as Mixed-Ligand Complexes with Hexafluoroacetylacetone and Tri-*n*-octylphosphine Oxide Using Solvent Extraction and Gas Chromatography

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## Abstract

The application of gas chromatography (GC) to the analysis of lanthanides as mixed ligand complexes with hexafluoroacetylacetone (HFAA) and tri-*n*-octylphosphine oxide (TOPO) is investigated. Thermogravimetric studies indicate that these complexes are volatile without decomposition at low temperature (100–200°C). The volatility of mixed chelates is found to increase with the decreasing radius of the trivalent lanthanide ion. Trivalent lanthanide ions are found to be quantitatively extractable with HFAA, a neutral donor, and TOPO as a mixed ligand complex in the pH range 2–7. The organic extract can be directly fed into a GC for separation and estimation. The optimum conditions for the estimation of lanthanides using GC are established. Chromatograms of lanthanides at different concentration ratios illustrate the possibility of the estimation of one lanthanide ion when as much as a 10-fold excess of other lanthanide ions is present in a mixture. Calibration curves of each of the individual lanthanides and their mixtures are studied in the concentration range 0.2–25 µg/mL.

## Introduction

Several metal chelates of hexafluoroacetylacetone (HFAA) have been shown to be volatile and can be resolved through gas chromatography (GC) (1,2). However, the solid chelates need to be prepared in anhydrous form and then dissolved in a suitable solvent prior to injection into a GC, which limits its application as an analytical technique.

Solvent extraction enables the quantitative extraction of metal chelates in an organic phase. However, HFAA forms hydrated chelates with rare earths, which are extracted poorly. Neutral donors such as tri-*n*-octylphosphine oxide (TOPO), tri-*n*-butyl phosphate (TBP), dibutyl sulphoxide (DBSO), etc. are known to increase the extraction percentage (3). There are reports (4,5) on GC of rare-earth mixed-ligand complexes with β-diketones and TBP-DBSO.

Systematic and detailed studies on the thermogravimetry and GC of mixed-ligand complexes of lanthanides with HFAA and TOPO revealed that they can be quantitatively extracted and estimated rapidly by integrating solvent extraction and GC. The results are presented in this paper. The solvent extraction efficiently separates the lanthanides from major matrix-interfering elements and allows the rapid preparation of volatile species, and GC permits the separation of individual lanthanides from mixtures for further estimation.

## Experimental

### Reagents

The lanthanide oxides (99.9% purity, Indian Rare Earths Ltd., Chatrapur, India) were dissolved in 0.01M diluted hydrochloric acid and standardized by titrating with ethylenediaminetetraacetic acid (EDTA) using xylenol orange as an indicator (6). Solutions of HFAA (0.1M, 98% purity, Fluka, Switzerland) and TOPO (92% purity, E. Merck, Darmstadt, Germany) were prepared in cyclohexane.

### Equipment

#### Thermogravimetric studies

Thermograms were obtained using a Perkin-Elmer (Norwalk, CT) DSC analyzer. The atmosphere over the sample was helium gas (purified by passing it through molecular sieves) and the flow rate was held constant at 60 mL/min throughout all experiments. The sample heating rate was 10°C/min, and efforts were made to keep the sample masses as similar as possible to maximize comparability.

### GC

An Amil Nucon GC 5700 with a flame ionization detector was used for the GC study. The GC column (150 cm × 3-mm i.d., stainless steel) supplied with the instrument was used for the preparation of Dexsil 300. The column was packed with 5 g of dry Chromosorb W (60–80 mesh) and soaked with a solution of

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9.45% Dexsil 300 in 56 mL of cyclohexane. The excess solution was drained off. SE-30 and QF-1 columns were similarly prepared. The analysis was conducted using a nitrogen flow rate of 50 mL/min, an injection port temperature of 280°C, and a detector temperature of 290°C.

### Solvent extraction

Solvent extractions were performed in a 50-mL separatory funnel. Five milliliters of the 0.01M lanthanide solution was placed in the separatory funnel, the acidity was adjusted to 0.01M hydrochloric acid, and the total volume was adjusted to 10 mL. To this aqueous phase, 10 mL each of 0.1M HFAA and 0.1M TOPO solutions in cyclohexane were added and equilibrated for 10 min. After phase separation, the organic phase was separated and dried over anhydrous sodium sulfate.

The organic phase (containing lanthanides in the range of La 347.25 to Lu 437.45 µg/mL) was diluted appropriately with cyclohexane to span the respective working concentration range (0.2–25 µg/mL). To determine the percent extraction of each lanthanide as HFAA–TOPO mixed-ligand system, separate extractions were carried out, and the lanthanide present in the aqueous and organic phases (after back-extraction with 2M HCl) was determined by titration with EDTA using xylenol orange as an indicator.

### Preparation of solid mixed ligand chelates

The organic phase of the lanthanide mixed-ligand complex after solvent extraction as described above procedure was separated, washed with 0.01M NaOH, separated again, and dried on anhydrous sodium sulfate. It was then shaken with an equal amount of diethylether. The organic phase was evaporated, leaving a viscous oil from which the solid mixed-ligand chelates of lanthanides with HFAA and TOPO were isolated. The solid mixed chelates were purified by recrystallization from a mixture of water–methanol (9:1).

### Preparation of calibration curves

In each case, 1.0-µL samples of the lanthanide complexes were injected into the GC. Three to five repetitions of each sample were performed, and the average of the area under the GC peak as determined by the integrator was plotted against the sample concentration.

## Results and Discussion

### Synthesis and characterization of mixed-ligand complexes of lanthanides with HFAA and TOPO

The synthesis, physical properties, and thermogravimetric data of the binary complexes of lanthanides with HFAA, including their GC behavior, have been previously reported (1). Trivalent lanthanide ions that are poorly extracted (< 10%) either by HFAA or TOPO alone can be quantitatively extracted in the presence of both,

exhibiting synergistic extraction (Figure 1). The corresponding mixed-ligand complexes were isolated by solvent extraction, and

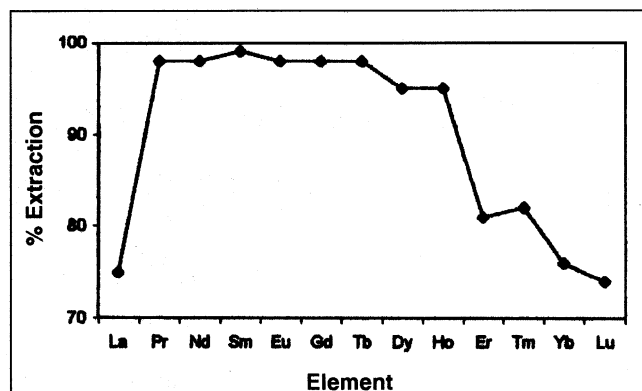


Figure 1. Extraction of trivalent lanthanide ions as HFAA–TOPO mixed-ligand complexes.

Table I. Color and Melting Points of Lanthanide Mixed-Ligand Complexes with HFAA and TOPO

Mixed chelate Ln(HFAA) <sub>3</sub> ·2TOPO	Color	Melting point (°C)
Lu(HFAA) <sub>3</sub> ·2TOPO	white	110–115
Yb(HFAA) <sub>3</sub> ·2TOPO	white	125–132
Tm(HFAA) <sub>3</sub> ·2TOPO	white	140–145
Er(HFAA) <sub>3</sub> ·2TOPO	pink	158–164
Ho(HFAA) <sub>3</sub> ·2TOPO	cream white	172–178
Dy(HFAA) <sub>3</sub> ·2TOPO	cream white	180–185
Tb(HFAA) <sub>3</sub> ·2TOPO	light yellow	165–180
Gd(HFAA) <sub>3</sub> ·2TOPO	white	170–175
Eu(HFAA) <sub>3</sub> ·2TOPO	light yellow	175–178
Sm(HFAA) <sub>3</sub> ·2TOPO	cream white	205–210
Nd(HFAA) <sub>3</sub> ·2TOPO	lavender	208–210
Pr(HFAA) <sub>3</sub> ·2TOPO	light green	210–215
La(HFAA) <sub>3</sub> ·2TOPO	white	205–210

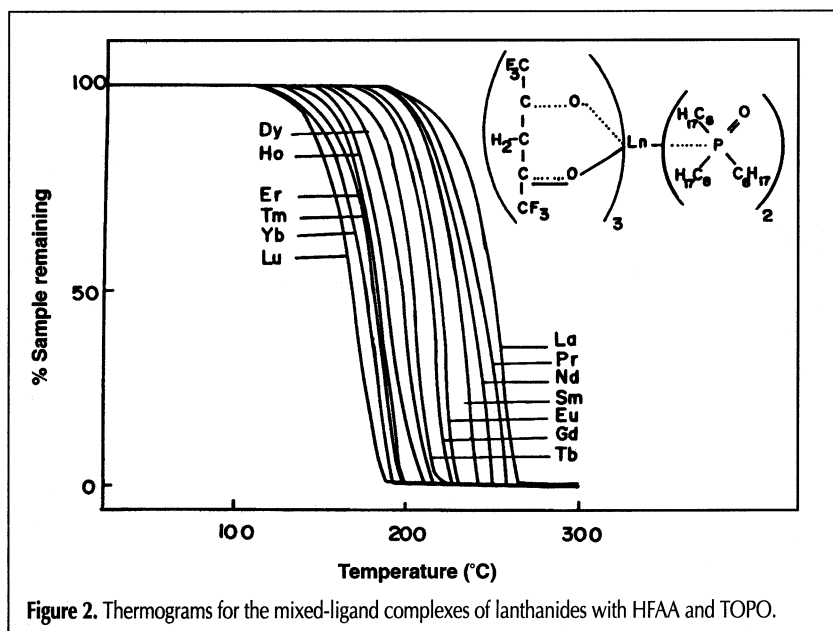


Figure 2. Thermograms for the mixed-ligand complexes of lanthanides with HFAA and TOPO.

information on their color and melting points is presented in Table I. In general, mixed complexes have lower melting points than their corresponding binary complexes.

#### Thermogravimetric studies of mixed-ligand complexes of lanthanides

The thermogravimetric data of the mixed-ligand complexes of lanthanides with HFAA and TOPO were obtained (Figure 2). The thermograms indicate that all the mixed complexes volatilize completely without decomposition between 180 and 300°C and at a 5–10% lower temperature than the corresponding binary complex (1). Examining the temperature at the midpoint of weight loss shows significant differences in the volatility of the mixed-ligand complexes of lanthanides. The heavier lanthanides were found to be volatilized at lower temperatures than their lighter neighbors. The differences in volatility can be correlated with the ionic radius of the trivalent lanthanides (as is also observed in binary complexes) and exploited for the separation of individual lanthanide ions by GC.

#### Optimum GC conditions for the separation of lanthanides

##### Stationary phase

The liquid phase Dexsil 300 was found to provide reproducible

chromatograms without any prior conditioning of the columns when compared with SE-30 and QF-1. Longer retention times and less-reproducible values over repeated runs were observed for SE-30 and QF-1, which may be caused by a greater interaction between Ln-HFAA-TOPO chelates and column materials.

##### Column temperature

All of the mixed chelates of the studied lanthanides were satisfactorily eluted at 220°C, but limited separations can be performed under isothermal conditions. However, for the separation of difficult mixtures, temperature programming in the range of 172–290°C (linearly increased at a rate of 6°C/min) was adopted.

#### Quantitative Studies of lanthanide mixed chelates with HFAA and TOPO

##### Detection limits

Detection limit and detector response were determined for most of the lanthanide ions, and the results are presented in Table II. The detection limit was the amount of mixed-ligand complex necessary to give a chromatographic peak response equal to or greater than three times the background.

**Table II. Linear Ranges of Calibration Graphs for Lanthanide Mixed-Ligand Chelates with HFAA and TOPO**

Lanthanide	Ionic radii (Å) <sup>13</sup>	Retention time (min)	Retention volume (mL)	Linear range (µg/mL)	Column temperature (°C)	Detection limit (µg/mL)	Response factor (10 <sup>-5</sup> integ. counts/µg)
Lu	0.848	4.0	0.594	0.5–15	205	0.30	3.15
Yb	0.858	4.1	0.609	1.0–2.0	215	0.27	3.75
Tm	0.869	4.2	0.624	0.5–15	225	0.30	4.10
Er	0.881	4.5	0.668	0.5–20	220	0.22	7.20
Ho	0.894	4.8	0.713	0.5–15	215	0.22	4.55
Dy	0.908	5.2	0.772	1.0–25	220	0.27	5.70
Gd	0.938	5.9	0.876	1.0–25	225	0.35	2.8
Eu	0.950	6.5	0.965	1.0–20	230	0.22	5.75
Sm	0.964	7.3	1.084	0.2–10	240	0.012	24.75
Nd	0.998	9.0	1.336	0.5–15	255	0.27	4.15
Pr	1.013	10.6	1.574	0.5–20	260	0.30	2.30
La	1.061	11.9	1.767	0.5–25	260	0.60	0.95

**Table III. Determination of Individual Lanthanides as HFAA-TOPO Mixed-Ligand System**

Lanthanide	Amount taken (µg)		Amount found* (µg)		Relative error (%)		Standard deviation	
Lu	4.38	8.75	4.32	8.69	-1.36	-0.68	0.025	0.080
Yb	8.65	4.23	8.57	4.17	-0.92	-1.42	0.041	0.057
Tm	8.45	4.18	8.61	4.29	+1.89	+1.41	0.030	0.043
Er	8.36	4.18	8.30	4.08	-0.71	-2.39	0.045	0.070
Ho	4.13	8.25	4.05	8.12	-1.93	-1.45	0.077	0.084
Dy	8.13	12.19	8.06	12.04	-0.86	-1.23	0.065	0.066
Gd	7.93	7.86	7.87	7.82	-1.52	-0.50	0.060	0.090
Eu	7.60	3.80	7.54	3.73	-0.78	-1.84	0.055	0.048
Sm	7.52	3.76	7.55	3.68	+0.39	-2.12	0.080	0.041
Nd	10.81	7.21	10.72	7.26	-0.83	+0.69	0.099	0.057
Pr	7.05	3.53	7.00	3.58	-0.70	+1.41	0.070	0.090
La	6.96	3.48	6.98	3.43	+0.28	+1.43	0.050	0.053

\* Average of five determinations.

### Preparation of calibration curves

The retention time, column temperature, and linear range of lanthanide ions as mixed-ligand complexes are also presented in Table II. Calibration curves of each individual lanthanide exhibit linearity in the range of 0.2–25 µg/mL. The analysis of unknown solutions of individual lanthanides is presented in Table III.

### Separation Studies

Calibration curves for use in the determination of mixtures of lanthanides were also prepared by the same method as previously mentioned using stock solutions of lanthanides in ratios of 0.5:1.5 and 1:1. This procedure was used in order to correct for any peak overlap, and the results are presented in Table IV.

The mixed complexes containing TOPO exhibited longer retention times than their corresponding binary complexes, indicating greater column interaction. The increased polar characteristics imparted on the complexes by the more polar TOPO moiety and the increased size of mixed complex may be responsible for these differences. Chromatograms for the mixtures of the lanthanides are shown in Figure 3. They indicate the applicability of GC for the separation and estimation of lanthanides.

Because of close retention times, the complete resolution of the pairs Lu–Yb (resolution factor  $R = 0.58$ ), Yb–Tl ( $R = 0.62$ ), and Tl–Lu ( $R = 0.72$ ) could not be achieved. Mixtures of lutecium and gadolinium at different concentration ratios were separated by GC, and the corresponding chromatograms (Figure 4) illustrate the separation of the lanthanides when as much as a 10-fold excess of one lanthanide was present in the mixture. It should also be noted that at excessively high concentrations, the peak shape becomes broader, which may be due to column overloading and is one of the limiting factors for the operational concentration range.

### Conclusion

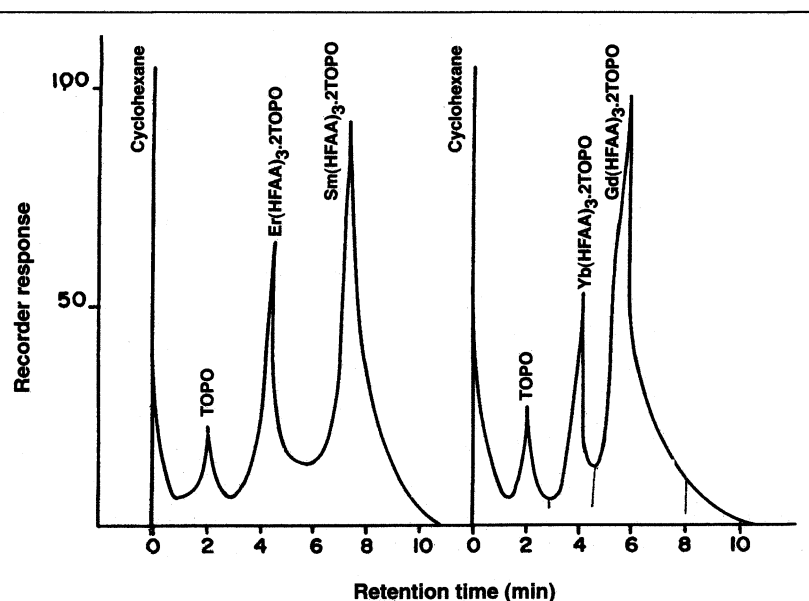
The present method of separation and preconcentration of lanthanides from matrix elements by a solvent extraction procedure, separation into individual lanthanides by GC, and estimation by FID detection is very rapid in comparison with other chromatographic techniques, such as high-performance liquid chromatography (7,8) and ion-exchange chromatography (9), and it is comparable in selectivity and sensitivity with these methods. The use of the solvent extraction for the separation of Ln–HFAA–TOPO mixed-

ligand complexes (suitable for GC) enables the preconcentration and separation of the analyte from the interfering matrix

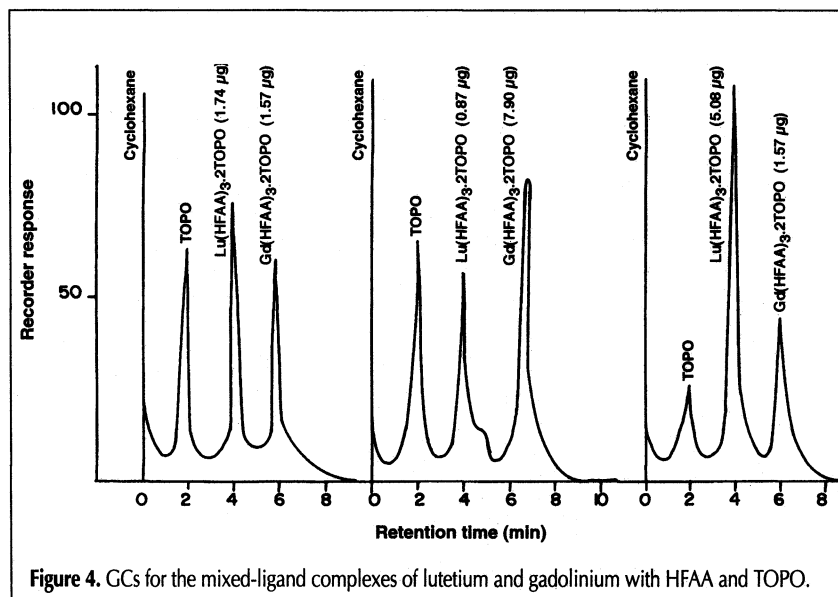
**Table IV. Determination of Mixtures of Lanthanides Using the HFAA–TOPO Mixed-Ligand System**

Lanthanide	Amount taken (µg)	Amount found* (µg)	Relative error (%)	Standard deviation
Lu	13.13	13.01	-0.91	0.092
Gd	3.93	3.87	-1.53	0.052
Lu	8.75	8.84	+1.02	0.078
Gd	7.86	8.01	+1.90	0.045
Lu	4.38	4.24	-3.19	0.068
Gd	11.79	11.65	-1.19	0.097
Lu	13.13	13.26	+0.99	0.048
La	3.48	3.62	+4.02	0.067
Lu	8.75	8.84	+1.02	0.044
La	6.96	6.87	-1.29	0.058
Lu	4.38	4.25	-2.90	0.033
La	10.44	10.29	-1.43	0.084
Ho	12.38	12.54	+1.29	0.089
Gd	3.93	4.07	+3.56	0.067
Ho	8.25	8.17	-0.97	0.056
Gd	7.86	7.69	-2.16	0.044
Ho	4.13	4.41	+7.50	0.046
Gd	11.79	11.66	-1.10	0.055
Yb	12.98	12.65	-2.54	0.093
Pr	3.53	3.37	-4.53	0.078
Yb	8.65	8.53	-1.39	0.077
Pr	7.05	7.00	-0.70	0.059
Yb	4.33	4.26	-1.61	0.078
Pr	10.58	10.24	-3.21	0.043
Yb	12.98	12.75	-1.77	0.086
Eu	3.80	3.63	-4.47	0.076
Yb	8.65	8.57	-0.92	0.047
Eu	7.60	7.51	-1.18	0.032
Yb	4.33	4.20	-3.00	0.027
Eu	11.40	11.29	-0.96	0.078

\* Average of five determinations.



**Figure 3.** Gas chromatograms for the mixed ligand complexes of lanthanides with HFAA and TOPO.



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components after properly selecting the experimental conditions. Thus, the integration of solvent extraction with GC can be applied as a novel technique and rapid and selective method for the analysis of lanthanides present in complex matrices.

## Acknowledgments

The authors gratefully acknowledge the financial support provided by the Department of Atomic Energy, India, by means of an R&D project for executing this work.

Manuscript accepted June 18, 1998.