MONTANA STATE UNIVERSITY

Some spectral and chemical interferences on the determination of dysprosium, holmium and erbium by atomic absorption spectrophotometry

by Hans Christian Claassen

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIEHCE in Chemistry

Montana State University

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Abstract:
The spectral and chemical interference of the rare earth elements, and those elements in common association with rare earth ores upon perchloric acid dissolution, on the determination of dysprosium, holmium and erbium by atomic absorption spectrophotometry is reported. Some suggestions are made to aid the analyst in determining these rare earths in the presence of other rare earths A redox phenomenon based on electronic configuration is suggested to explain the rare earth element interference observed. This is believed to be a new approach to flame processes involving the rare earth elements.

SOME SPECTRAL AND CHEMICAL INTERFERENCES ON THE DETERMINATION OF DYSPROSIUM, HOLMIUM AND ERBIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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TABLE OF CONTENTS

		Page
	LIST OF TABLES	v
	LIST OF FIGURES	vi
	ABSTRACT	vii
I.	INTRODUCTION	1
II.	GENERAL CONSIDERATIONS	2
III.	EXPERIMENTAL	4
	A. Absorption Apparatus	4
	B. Instrumental Conditions	5
	C. Absorption Procedures	7
	D. Standard Solutions	7
IV.	RESULTS	9
	A. Spectral Interferences	9
	B. Chemical Interferences	11
	C. Analytical Potential	16
	D. Data	17
V.	SUMMARY	22
VI.	LITERATURE CITED	24

LIST OF TABLES

Table		Page
I.	Optimum Instrumental Conditions	7
II.	Spectral Interferences on Dysprosium, Holmium and Erbium in Units of Percent Transmittance	10
III.	Chemical Interferences of Non Rare Earth Metals on Dysprosium, Holmium and Erbium	12
IV.	Chemical Interferences of Rare Earth Elements on Dysprosium, Holmium and Erbium	13

LIST OF FIGURES

Figure		Page
1.	Last Stage Tuned Amplifier	6
2.	Effect of Rare Earth Interferents on the Absorbance of 200 ugm/ml Erbium	14
3.	Effect of Varying Amounts of Interferent on 250 ugm/ml Dysprosium	18
4.	Effect of Varying Amounts of Interferent on 300 ugm/ml Holmium	18
5.	Effect of Varying Amounts of Interferent on 200 ugm/ml Erbium	19
6.	Effect of 1000 ugm/ml Interferent on Varying Concentrations of Dysprosium	20
7.	Effect of 1000 ugm/ml Interferent on Varying Concentrations of Holmium	20
8.	Effect of 1000 ugm/ml Interferent on Varying Concentrations of Erbium	21

ABSTRACT

The spectral and chemical interference of the rare earth elements, and those elements in common association with rare earth ores upon perchloric acid dissolution, on the determination of dysprosium, holmium and erbium by atomic absorption spectrophotometry is reported. Some suggestions are made to aid the analyst in determining these rare earths in the presence of other rare earths.

A redox phenomenon based on electronic configuration is suggested to explain the rare earth element interference observed. This is believed to be a new approach to flame processes involving the rare earth elements.

INTRODUCTION

It has been demonstrated (19) that at least some of the rare earth elements can be analytically determined by means of atomic absorption spectrophotometry. It is furthermore evident that since the rare earth elements are chemically similar (20, 21, 26) they will of necessity be determined in presence of each other, and a study of the spectral and chemical (cationic) interferences will be necessary.

Historically there has been much speculation as to flame processes governing observed chemical interferences. Most investigators have proposed the formation of refractory compounds to explain the observed interference (18, 24, 25). In the determination of metals which form refractory oxides, such as the rare earths, few metal atoms are available for absorption or emission. A fuel-rich oxygen/acetylene flame has been successfully used in lowering the detection limits of rare earth elements by both atomic absorption (19) and emission (3, 7) spectrophotometry. This method owes its success to the proposed (7) reaction

$$REO + C = RE^{\circ} + CO \qquad (I)$$

Though this reaction is sufficient to explain the increased absorption (or emission) when only one rare earth element is present, it becomes inadequate when other rare earth elements are introduced.

GENERAL CONSIDERATIONS

The primary objective is to present empirical evidence of spectral and chemical interferences of rare earth elements in the determination of dysprosium, holmium and erbium by atomic absorption methods. In addition, chemical and spectral interference data will be given on those elements which are likely to occur with rare earth elements upon dissolution of their ores with perchloric acid[1].

It is expected that the spectral interference observed will be a function of the effective bandwidth of the monochromator (5) and any lines or bands of the interferent which might fall within this effective bandwidth. The effective bandwidth takes into consideration optical aberrations and is given by

$$B_e = X(S + .04) \qquad \text{(II)}$$

where B_e is the effective bandwidth at slit width S,

and X is the bandwidth at 1 mm slit width, which is empirically determined, and was obtained graphically (15).

Some authors have suggested that the dissociation energies of the lanthanide monoxides steadily decrease as the atomic number of the rare earth element increases (9,23), and others have implied that europium, thulium and ytterbium do not form stable monoxides (5,19). If one assumes equation I to be the reaction

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[1]The choice of associated elements was made with the help of Ryabchikov (17) and Dana (4) and based on the premise that mineral samples would be digested in perchloric acid as suggested by Vickery (20).

governing the concentration of absorbing species in the flame, one would expect the equilibrium constant of equation IV to be greater than the equilibrium constant of equation III, if the dissociation energy of RE_dO is greater than the dissociation energy of RE_iO.

$$RE_dO + C = RE_d^o + CO \qquad \text{(III)}$$

$$RE_iO + C = RE_i^o + CO \qquad \text{(IV)}$$

where RE_d represents the rare earth element to be determined

and RE_i represents the rare earth interferent.

The overall effect would be little change in the RE_d^o concentration, if the concentration of carbon is large (16) compared to lanthanide monoxide.

It is proposed, however, that an additional reaction occurs in the flame which increases the RE_d^o concentration, resulting in increased absorption. This reaction is

$$RE_i^o + RE_dO = RE_iO + RE_d^o \qquad \text{(V)}$$

and the extent to which it goes to the right will be governed by the relative reducing ability of RE_i, which in turn will be governed by its electronic configuration.

EXPERIMENTAL

Absorption Apparatus

Light Sources. The following Westinghouse hollow cathode lamps were used as light sources: dysprosium (WX5465), holmium (WX5487) and erbium (WX5486). The lamp power output was regulated by a constant-current power supply (Lambda Electronics Corporation, model 71-B).

Burner. Since a fuel-rich oxygen/acetylene flame was desirable in this investigation, a Beckman oxygen/hydrogen burner was used (#4020). It was thought that this burner would supply a flame of smaller total volume and more favorable geometry, therefore concentrating the atoms available for absorption in the light path (6). In addition, a saving in fuel cost was predicted as the 4020 burner did not allow as high a consumption as the standard 4030 (oxygen/acetylene) burner. It was hoped that the attendant decrease in solution consumption rate would be offset by the aforementioned advantages, yielding nearly the same absorption calibration curves reported by Skogerboe (19).

Monochromator. A Beckman model DU quartz spectrophotometer was used as a monochromator.

Photodetector and Power Supply. An RCA IP28 photomultiplier tube was used, coupled with a power supply described by Box and Walsh (2) and modified by replacing British tubes with American

equivalents.

Amplifier. An AC tuned amplifier was used to amplify the signal from the phototube. This amplifier was originally described by Kalmus and Sanders (12), modified as reported by Skogerboe (19) and the third stage remodified as shown in Figure 1. Essentially, the amplifier is tuned to receive a 39 cycle signal, rejecting both 120 cycle signal from artificial light/power supply, and stray signals originating in the flame. The amplifier has a DC output for a recorder.

Recorder. A Bristol recorder, model 1PH560, with a 0-10 millivolt span full-scale was used for all measurements.

Instrumental Conditions

Since a different burner than reported by Skogerboe (19) was used, burner parameters had to be redetermined. Reported values for hollow cathode current and phototube voltages were utilized; the maximum oxygen flow rate, commensurate with dependable burner operation, set; the fuel flow rate and D (height above burner tip) varied to attain the absorption maxima. The conditions chosen, summarized in Table I, reflect essentially the same calibration curves reported by Skogerboe, even though the total flow rate is lower. This is brought about by the better flame geometry produced by the particular burner used.

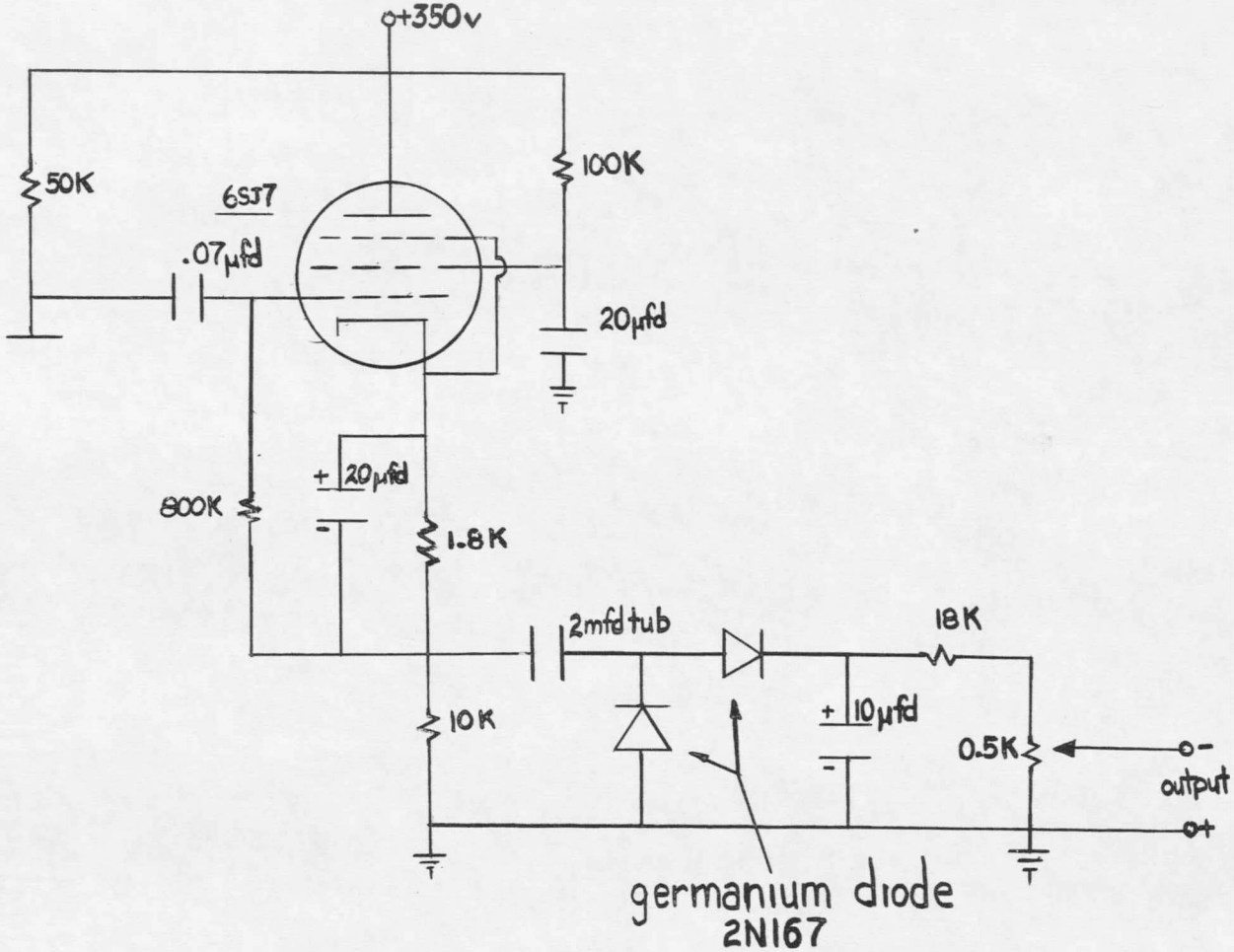

Figure 1. Last stage tuned amplifier

Table I. Optimum Instrumental Conditions

Element	Oxygen/Fuel Rep'd.	Oxygen/Fuel Found	O + F(ml/min) Rep'd.	O + F(ml/min) Found	D (mm) Rep'd.	D (mm) Found	Lamp Current (ma)	PM Volts	Slit mm
Dy	.80	.90	7500	6000	30	24	18	900	.01
Ho	.75	.90	7500	6000	30	25	20	900	.01
Er	.80	.90	7500	6000	30	26	15	900	.01

Absorption Procedures

Absorption measurements were made by setting the monochromator slit to its minimum width (.01), focussing on the absorption line and, by adjusting the amplifier gain, setting the recorder to read I_o with a blank in the flame. The absorption intensity, I, was then read with a sample solution aspirated into the flame. In general, each determination was made in triplicate.

Standard Solutions

All cations investigated were prepared as the perchlorates[2] and dissolved in absolute ethanol. Stock solutions

[2]The vanadium and aluminum solutions were prepared from the chloride salts of these metals. Corrections were made for the effect of chloride when necessary.

containing 10,000 micrograms per milliliter[3] of all metals were prepared. These solutions were diluted as required in absolute ethanol.

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[3] A common error appears to occur in transferring concentration calculations from aqueous solutions to alcohol solutions. In aqueous media, ppm is approximately equal to micrograms/ml; but in alcohol solutions an error of approximately 21% is introduced by making the assumption 1 gm EtOH = 1 ml at room temperature. It is suspected that much of the concentration information in the literature is in error.

RESULTS

Spectral Interferences

Although concentrated solutions of the rare earths, and metals associated with rare earth elements, generally yield no absorption at the three analytical wavelengths investigated, varying amounts of emission were passed through the monochromator and some of this emission signal was not rejected by the tuned amplifier; thus, an effective spectral interference was observed. It will be seen in Table II that, in general, spectral interference decreased as effective monochromator bandwidth decreased. The exceptions to this rule occur whenever emission lines lie close to the analytical wavelengths.

In Table II spectral interference values are listed, rounded to the nearest one-half scale division. One scale division is equivalent to one percent transmittance. Positive values indicate emission, negative values indicate absorption.

Table II. Spectral Interferences on Dysprosium, Holmium and Erbium in Units of Percent Transmittance

Interferent 10000 ugm/ml	Element Sought Dy 4211 A B_e=6.25 A	Ho 4103 A B_e=5.65 A	Er 4008 A B_e=5.25 A
La	0	0	0
Ce	+0.5	+0.5	+1.0
Pr	+1.5	+1.0	0
Nd	+1.5	+1.0	0
Sm	+1.0	+1.0	0
Eu	+1.0	+1.0	0
Gd	+0.5	+1.0	0
Tb	+2.0	+2.0	0
Dy	-	+1.0	0
Ho	+1.0	-	0
Er	+2.0	0	-
Tm	+1.5	0	0
Yb	+0.5	+0.5	0
Lu	+1.5	0	-0.5
Y	+2.5	+1.5	0
Be	+3.0	+2.0	0
Na	0	0	0
Ca	+3.0	+1.5	0
Fe	+2.0	+1.5	0
Al	+1.5	+1.0	0
In	+0.5	+4.0	0
V	+2.5	+4.5	0
Th	+0.5	+0.5	0
U	0	+0.5	0

Chemical Interferences

Since it was hoped that information on the behavior of the rare earths in the flame could be obtained, the chemical interference data are presented in two parts. The first part will be a purely tabular compilation of non rare earth interferent data (Table III) while the second part, dealing with rare earth element interferents, will be presented both tabularly (Table IV) and graphically (Figure 2).

In support of the hypothesis that equation V governs the enhancement evidenced in Table IV and Figure 2, the following is given.

The estimated oxidation potentials of the rare earth elements in aqueous media (14) reflect a decrease in reducing ability[4] with increasing atomic number. It appears to be reasonable to expect this trend to be carried through to the conditions of the flame since, from Figure 2, there is a general decrease in enhancement (a decrease in the equilibrium constant of equation V) as atomic number increases. The failure of europium and ytterbium, and to a lesser extent samarium and thulium, to follow the general trend can be explained if electronic config-

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[4]The potentials given were for the reaction $RE^{o} = RE^{3+} + 3e^{-}$.

urations are taken into account.

Table III. Chemical Interference of Non Rare Earth Metals on Dysprosium, Holmium and Erbium

Interferent	Element Sought all values given in units of ΔA[5]		
1000 ugm/ml	Dy 250ugm/ml	Ho 150ugm/ml	Er 200ugm/ml
Y	+.039	+.002	+.030
Be	-.063	-.041	-.069
Na	-.148	-.077	-.182
Ca	-.042	-.030	-.062
Fe	-.028	-.014	-.026
Al	-.209	-.080	-.242
Th	+.054	+.020	+.067
U	-.009	-.019	-.034

[5] ΔA represents the difference in absorbance value between the standard rare earth solution alone and the interferent solution, containing a concentration of element to be determined equivalent to that of the standard rare earth solution.

Table IV. Chemical Interference of Rare Earth Elements on Dysprosium, Holmium and Erbium

Interferent 1000 ugm/ml	Element Sought all values given in units of A Dy 250ugm/ml	Ho 300ugm/ml	Er 200ugm/ml
La	+.070	+.030	+.080
Ce	+.069	+.031	+.071
Pr	+.051	+.022	+.059
Nd	+.049	+.024	+.059
Sm	+.021	+.013	+.034
Eu	-.007	-.023	+.003
Gd	+.036	+.015	+.041
Tb	+.055	+.010	+.054
Dy	---	+.015	+.049
Ho	+.053	---	+.053
Er	+.051	+.013	---
Tm	+.046	+.002	+.040
Yb	+.033	+.006	+.033
Lu	+.043	+.010	+.045

It is known that particularly stable electron configurations are reached when electron "shells" are either filled or half-filled (eg 10,14). This is true of the lanthanides, where, since the well shielded 4f energy levels are being filled, there is little difference in chemical properties except when these stable configurations are reached (14,21,26). Stable half

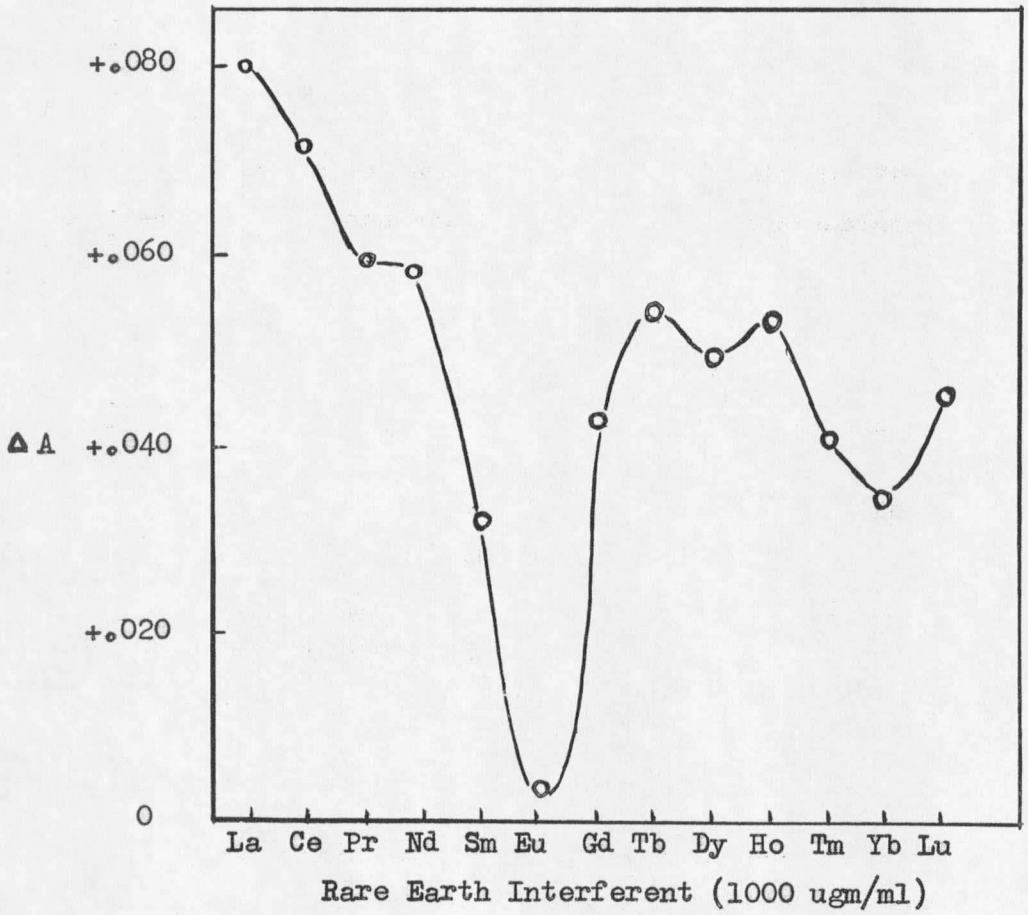

Figure 2. Effect of Rare Earth Interferents on the Absorbance of 200 ugm/ml Erbium

filled or filled 4f energy levels would exist only for Sm(I), Eu(II), Gd(III) $4f^7$ configuration; Tm(I), Yb(II), Lu(III) $4f^{14}$ configuration. The corresponding monoxide species would then be SmO^-, EuO, GdO^+, TmO^-, YbO, LuO^+. In a reducing flame, such as the one used, It is expected that the electron concentration would be such as to allow very few positive ions to exist, thus reducing the liklihood of GdO^+ and LuO^+ as significant constituents in the fuel-rich oxygen/acetylene flame. The configurations of the neutral atoms Eu(0) $4f^7 6s^2$ and Yb(0) $4f^{14} 6s^2$ are also expected to have increased stability.

The consequences of the postulated existence of these species are as follows.

(1) The stable oxide species of samarium, europium, thulium and ytterbium would inhibit equation IV from going to completion, thus bringing about a lower concentration of RE_i^o available for equation V and hence fewer RE_d^o for excitation. This effect would be evidenced in a lowering of enhancement (Figure 2).

(2) The existence of stable neutral atoms of europium and ytterbium would further inhibit equation V and cause an increased lowering of RE_d^o as compared to the effect evidenced by other, less stable, species.

The enhancements measured show that a change in RE_d^o concentration of as much as twenty percent is taking place. This is

not unreasonable in the light of the proposed reaction mechanism if, as is estimated, 10^9 collisions per second occur between RE_i^o and RE_dO[6] (8).

Analytical Potential

It would seem that with the serious chemical interferences evidenced an actual analysis of contaminated rare earth element would be difficult. In order to ascertain if a technique similar to the radiation buffer technique[7], which is commonly employed to suppress ionization in samples with low ionization potentials (5), could be used, fixed concentrations of RE_d containing varying concentrations of interferent were run. Some of the results are presented in Figures 3-5. The leveling out of the interference is evident; the slight decrease in enhancement occurring at high concentrations of interferent may be due to a decrease in aspiration rate (caused by an increase in the viscosity of the solution) with a consequent lowering of the

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[6] In this calculation it was assumed that all RE_d was present as RE_dO, the transit time of an atom through the flame is about 10 milliseconds and the volume of the flame is 50 cc.

[7] ...addition of an easily ionizable element to an element which suffers from a certain degree of ionization itself, thus minimizing the effect of small amounts of easily ionizable element which might have been present in the sample.

RE_d^o concentration in the flame[8]. It appears as if the addition of interferent, if the approximate concentration of interferent is known, would permit direct determination of rare earth element sought.

The effect of a constant concentration of interferent on varying concentrations of element sought was also investigated. The results are presented in Figures 6-8. Once again the critical concentration range (steepest ascent of curve) is evident. It would appear that saturation of the flame with RE_d^o occurs rather quickly. Viscosity effects are not evidenced, since all solutions are relatively dilute.

Data

The deviation at a ninety-five percent confidence level (11) for at least forty determinations of the standard solution of each element investigated (Dy, Ho, Er) is presented below.

250ugm/ml Dy : 3.4%
300ugm/ml Ho : 2.3%
200ugm/ml Er : 1.0%

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[8] Dysprosium does not behave in this manner, presumably because enhancement increases steadily at higher interferent concentrations, overshadowing the small viscosity effect. In the other elements investigated it appears that enhancement reaches a maximum and the viscosity effect takes over at high interferent levels.

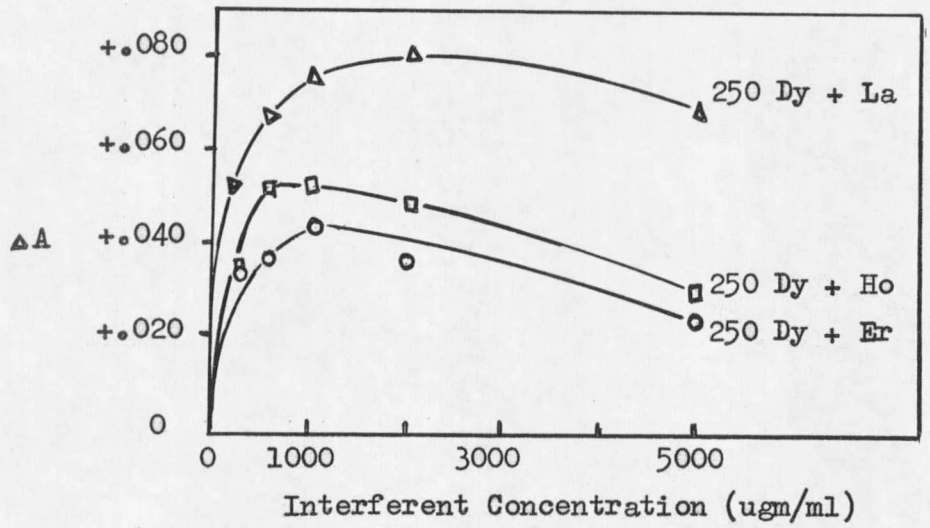

Figure 3. Effect of Varying Amounts of Interferent on 250 ugm/ml Dysprosium

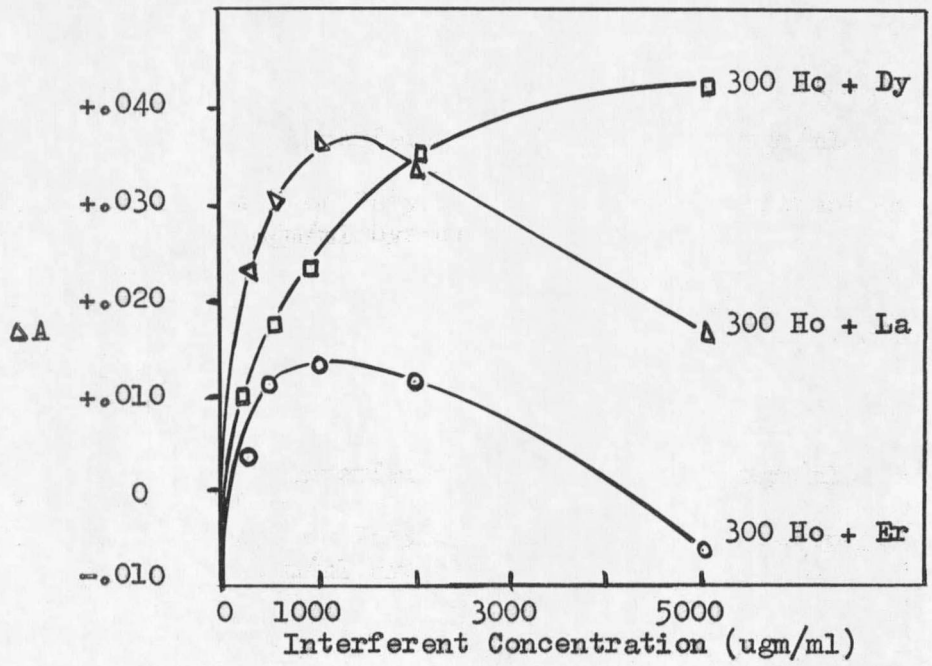

Figure 4. Effect of Varying Amounts of Interferent on 300 ugm/ml Holmium

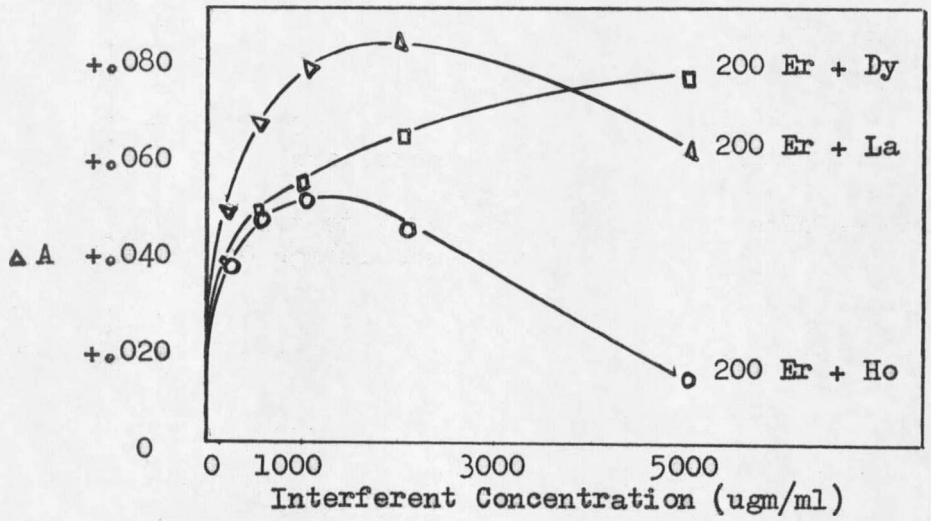

Figure 5. Effect of Varying Amounts of Interferent on 200 ugm/ml Erbium

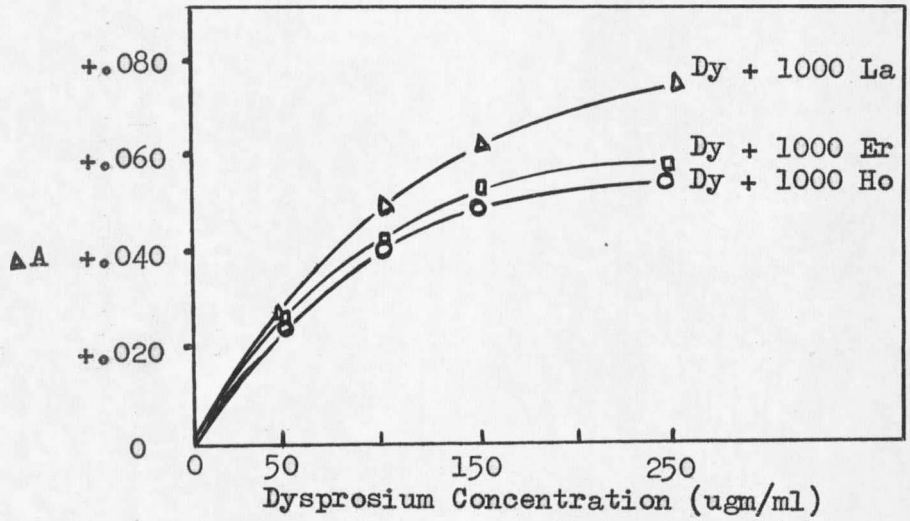

Figure 6. Effect of 1000 ugm/ml Interferent on Varying Concentrations of Dysprosium

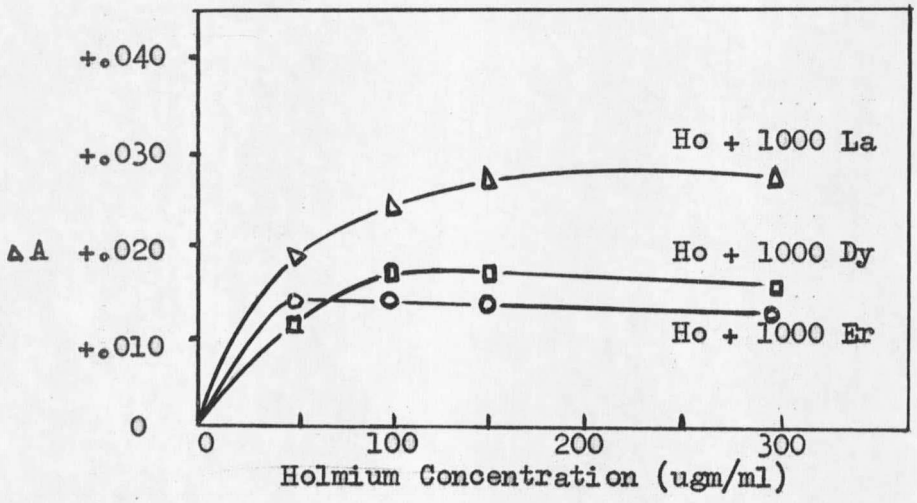

Figure 7. Effect of 1000 ugm/ml Interferent on Varying Concentrations of Holmium

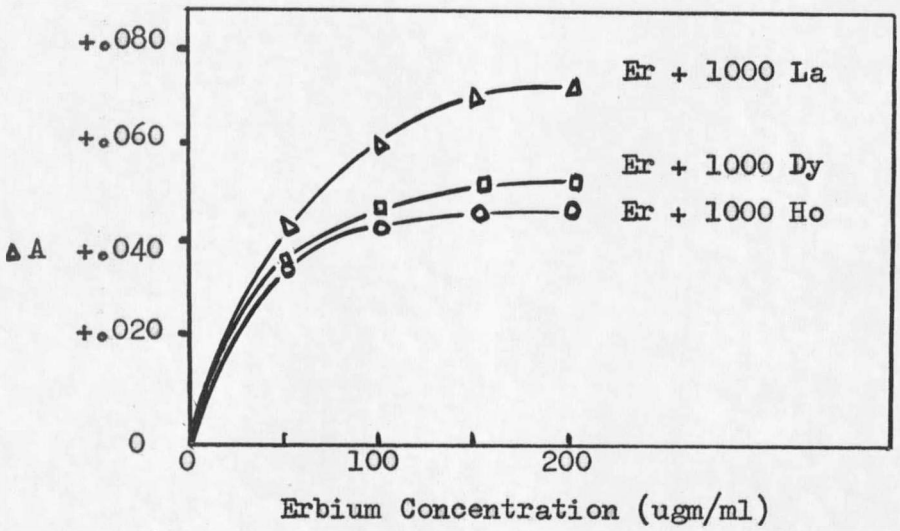

Figure 8. Effect of 1000 ugm/ml Interferent on Varying Concentrations of Erbium

SUMMARY

The feasibility of the determination of at least some of the rare earth elements in presence of each other has been demonstrated. It remains to be shown what the effect of many rare earth interferents on one element would be[9] and if procedures could be devised for direct analysis of ores. Elements such as aluminum have such a serious depressive effect that removal would appear to be the only recourse if reasonable detection sensitivities were to be maintained. It is possible that either the interferent or the element to be determined could be preferentially complexed by the addition of a complexing agent such as has been done in the case of the inhibition of calcium emission by phosphorous (24,25).

Consideration of dissociation energy phenomena alone appears to be grossly inadequate to explain these flame processes. Results other than those expected on the basis of previously proposed arguments (7,19) are obtained. A plausible, simple redox phenomenon has been proposed to explain the observations. With the determination of the oscillator strengths of the absorption lines, the use of a pre-mix burner reported by Kniseley, et

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[9]From the results on emission work reported by D'Silva (3) et al., who reported no interference when complex rare earth systems were analyzed, it is possible that interelement effects observed in a turbulent flame may be eliminated by the use of a pre-mix burner.

al. (7,13) and the use of a multipass optical system (1) to increase the sensitivity, the equilibrium constants for equations III-V should be determinable.

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