



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 SCIENCE 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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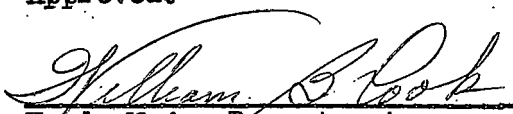
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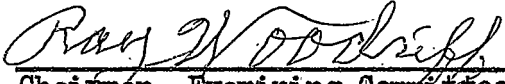
MASTER OF SCIENCE

in

Chemistry

Approved:


Head, Major Department


Chairman, Examining Committee


Dean, Graduate Division

MONTANA STATE COLLEGE
Bozeman, Montana

August, 1964

ACKNOWLEDGMENT

I would like to thank Drs. R. Woodriff and K. Emerson and also Mr. H. McLean for their suggestions and assistance.

To my wife Christine, my gratitude for her patience and cooperation.

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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.

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



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 acid¹.

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

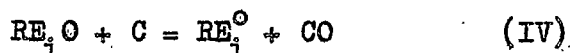
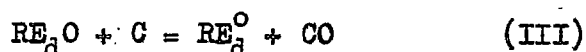
$$B_e = X(S + .04) \quad (\text{II})$$

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

¹The 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 .



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° 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° concentration, resulting in increased absorption. This reaction is



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.

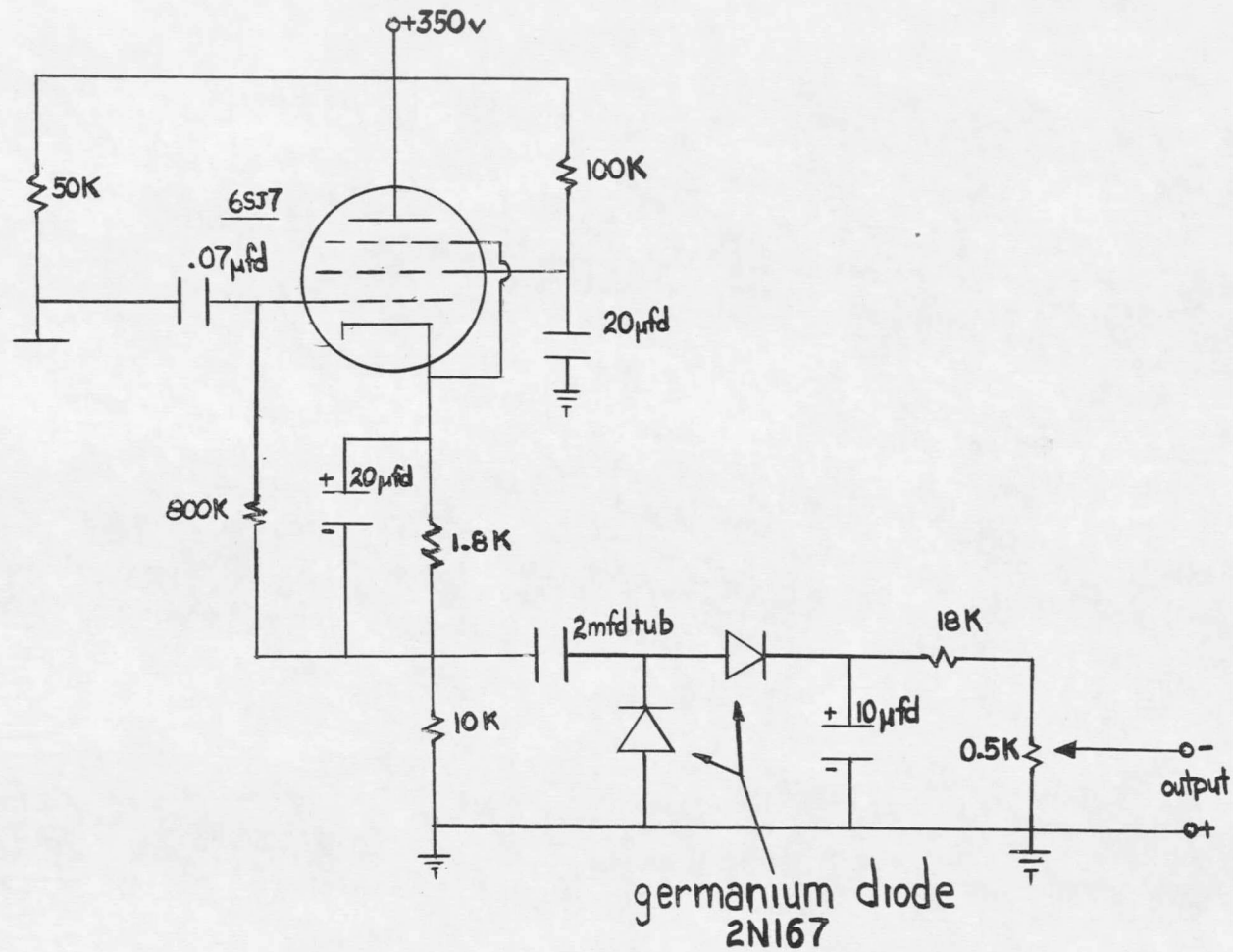


Figure 1. Last stage tuned amplifier

Table I. Optimum Instrumental Conditions

Element	Oxygen/Fuel		O + F(ml/min)		D (mm)		Lamp Current (ma)	PM Volts	Slit mm
	Rep'd.	Found	Rep'd.	Found	Rep'd.	Found			
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_0 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 perchlorates² and dissolved in absolute ethanol. Stock solutions

²The 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 milliliter³ of all metals were prepared. These solutions were diluted as required in absolute ethanol.

³A 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 interferences, 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 ability⁴ 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-

⁴The potentials given were for the reaction $RE^0 = RE^{3+} + 3e^-$.

urations are taken into account.

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

Interferent 1000 ugm/ml	Element Sought ⁵ all values given in units of ΔA		
	Dy 250ugm/ml	Ho 150ugm/ml	Er 200ugm/ml
Y	+0.039	+0.002	+0.030
Be	-0.063	-0.041	-0.069
Na	-0.148	-0.077	-0.182
Ca	-0.042	-0.030	-0.062
Fe	-0.028	-0.014	-0.026
Al	-0.209	-0.080	-0.242
Th	+0.054	+0.020	+0.067
U	-0.009	-0.019	-0.034

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	Element Sought		
	all values given in units of	A	
1000 ugm/ml	Dy 250ugm/ml	Ho 300ugm/ml	Er 200ugm/ml
La	+0.070	+0.030	+0.080
Ce	+0.069	+0.031	+0.071
Pr	+0.051	+0.022	+0.059
Nd	+0.049	+0.024	+0.059
Sm	+0.021	+0.013	+0.034
Eu	-0.007	-0.023	+0.003
Gd	+0.036	+0.015	+0.041
Tb	+0.055	+0.010	+0.054
Dy	---	+0.015	+0.049
Ho	+0.053	---	+0.053
Er	+0.051	+0.013	---
Tm	+0.046	+0.002	+0.040
Yb	+0.033	+0.006	+0.033
Lu	+0.043	+0.010	+0.045

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

