Study of the optimum conditions for the analysis of some rare earths by atomic absorption methods
by Roger Kenneth Skogerboe

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University

Abstract:
The principle atomic absorption wavelengths for europium, thulium, ' ytterbium, dysprosium, holmium, erbium and samarium have been determined and the applicability of atomic absorption for the quantitative analysis of these elements has been evaluated. Detection limits comparable to those exhibited by flame spectrpphotometric methods have been observed.

It is furthermore evident that the absorption wavelengths are not subject to spectral interference by other members of the lanthanon series.

It is demonstrated that atomic absorption determinations of analytical utility can be accomplished for europium, thulium, and ytterbium by using an oxyhydrogen flame as the absorption line source.

Other experiments are reported for solvent effects on flame excitation. It is shown that solvent effects on the rare earth flame excitation do not yield predictable enhancements.

A statistical design method for determining optimum experimental parameters is used and compared with the more common technique. It is established that the statistical technique is preferable for the systems investigated.

The excitation and absorption data are shown to provide semiquanti-tative support for a chemiluminescent mechanism proposed by Fassel, Curry, and Khiseley (15).

STUDY OF THE OPTIMUM CONDITIONS FOR THE ANALYSIS OF SOME RARE EARTHS BY ATOMIC ABSORPTION METHODS

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RODNEY K. SKOGERBOE

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Chemistry

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ABSTRACT

The principle atomic absorption wavelengths for europium, thulium, ytterbium, dysprosium, holmium, erbium and samarium have been determined and the applicability of atomic absorption for the quantitative analysis of these elements has been evaluated. Detection limits comparable to those exhibited by flame spectrophotometric methods have been observed. It is furthermore evident that the absorption wavelengths are not subject to spectral interference by other members of the lanthanon series.

It is demonstrated that atomic absorption determinations of analytical utility can be accomplished for europium, thulium, and ytterbium by using an oxyhydrogen flame as the absorption line source.

Other experiments are reported for solvent effects on flame excitation. It is shown that solvent effects on the rare earth flame excitation do not yield predictable enhancements.

A statistical design method for determining optimum experimental parameters is used and compared with the more common technique. It is established that the statistical technique is preferable for the systems investigated.

The excitation and absorption data are shown to provide semiquantitative support for a chemiluminescent mechanism proposed by Fassel, Curry, and Kniseley (15).

INTRODUCTION

The series of rare earth elements are recognized as being similar in chemical properties (14,38,39). Consequently, specific quantitative analyses can be made on only a few members of this series by non-instrumental techniques. In spite of this chemical similarity, the lanthanons[1] do have characteristic spectrochemical features arising from transitions between the 4f electronic energy states (14,15,28,30,39). As a result, the most successful methods for their determination have usually been spectrochemical in nature. The major objections to these methods derive from the high degree of spectral interference often observed, the complex sample preparation procedures, and the cost of the required instrumentation.

In 1955, Walsh realized the latent potential of atomic absorption and developed the first useful analytical instrumentation (5,37,40). Applications of the method have shown that there are marked advantages in comparison to emission techniques (1,9,10,13,23,25,29,33,34,37,41,42). The most significant of these are: a decrease in spectral interference, lowering of detection limits, reduction of temperature dependence, minimization of interelement effects and a lower cost of instrumentation.

These observations, and the report by Fassel, Curry, and Kniseley (15) that the rare earths can be excited in a fuel-rich oxyacetylene

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[1] Confusion often arises from names applied to this series of elements. In general, the rare earth series and the lanthanide series are the same (atomic numbers 57 through 71), while the lanthanon series consists of the rare earths plus yttrium and scandium.

flame, indicate that atomic absorption may be utilized with advantage for the quantitative determination of the rare earths. This report gives the detailed results of experiments designed to determine the optimum techniques and parameters for using atomic absorption as an analytical method for the rare earths.

GENERAL CONSIDERATIONS

To observe atomic absorption, a steady beam of light containing the emission spectrum of the element to be determined is passed through a flame containing an atomic vapor of the same metal (see Figure 1, page 9). The metal atoms in the flame absorb at characteristic wavelengths (identical with the emission wavelengths) and the degree of absorption is a measure of the number of atoms present (33,34,40). Under ideal conditions, the general absorption equation holds:

$$I_\lambda = I_o \, e^{-K_\lambda l} , \qquad (1)$$

where I_o = initial light intensity at wavelength λ,

I_λ = intensity after absorption at wavelength λ,

K_λ = apparent absorption coefficient, and

l = absorption path length.

There are three principle factors influencing the absorption process: natural line width (that due to the uncertainty principle), Doppler broadening, and external effects such as pressure and Stark broadening. If only Doppler broadening is important, the absorption coefficient is

$$K_\lambda = \frac{2\lambda^2}{D_\lambda} \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{\pi e^2}{mc^2} N_\lambda f, \qquad (2)$$

where D_λ = Doppler bandwidth at wavelength λ,

e = electronic charge,

m = electron mass,

c = velocity of light,

N_λ = number of atoms per unit volume capable of absorbing in the range λ to $\lambda + \delta\lambda$, and

f = oscillator strength; defined as the average number of electrons per atom which can be excited by the incident radiation.

Since D_λ is proportional to $(T)^{\frac{1}{2}}$ (17,40), K_λ is relatively insensitive to temperature and the degree of absorption is a linear function of concentration. In practice, the most useful absorption wavelengths are those associated with transitions from the ground state of the neutral atom since their oscillator strengths are usually largest (13,28,30,33,36,40).

Other authors (9,10,13,23,25,29,34) have observed that the flame conditions maximizing atomic emission also maximize atomic absorption. Prior to the work of Fassel et al (15), only europium, thulium, and ytterbium had been observed to emit analytically useful atomic spectra in a flame. The other lanthanons form stable monoxides in this medium and the energies of normal flames are insufficient for dissociation (12, 14,15,17). By using a fuel-rich oxyacetylene flame and an organic solvent however, advantage is taken of the phenomenon known as chemiluminescence[2] to promote dissociation of the oxides and subsequent excitation of the free metal atoms (15,19). The reports by Fassel et al (15), Gilbert (19), and others (9,10,13,23,25,29,34) indicated that information about the mode of production of free atoms in the flame could be obtained by studying excitation. Flame emission characteristics of some of the rare earths are considered later.

Excitation in a flame has been thoroughly discussed elsewhere (e.g. 12). The complex overall process depends on variables such as: temperature, the geographic region of the flame being examined, the sample feed

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[2] A chemical reaction which may lead to the formation of an atom or molecule in an electronically excited state from which radiation may occur.

rate and the solvent used for sample aspiration. By controlling the oxygen to fuel flow rate ratio (O/F) and the total flow rate of oxygen plus fuel (O + F), one can reproducibly obtain a particular temperature, flame geometry, and sample feed rate. Hence, the excitation conditions can be optimized by varying the three factors: O/F, O + F and D′(the vertical position in the flame from which the light sample is taken). A definitive explanation of the role of the sample solvent in the excitation process has eluded many investigators (12,13,24,34), but it does significantly affect the temperature, the sample feed rate, the droplet size distribution (32), and the flame geometry. The relative merits of various solvents will be discussed later. The three variables defining the flame are functionally related and thus exhibit interdependence. Box (3) has pointed out that when interactions among variables are substantial, the classical method of varying only one factor at a time (single-factor design) requires a large number of experiments and may lead to a false maximum. In 1951, Box and Wilson (4) advanced a statistical experimental design method (response surface method) conceived to minimize these problems. Complete discussions of the method have been presented (3,4,8,11, 43,44,45), thus only a summary description follows.

The experimentation proceeds in two phases. First, the method of steepest ascent (3,4,8,11) is used to determine the approximate variable levels required to maximize the response. In essence, factorial experimentation[3] is used to calculate linear equations relating the response

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[3] In this type of design, the effects of several factors are investigated simultaneously.

to the variables. These equations indicate the variable level changes required to approach the maximum. Subsequent experiments are moved in the directions indicated until the linear coefficients become small or undergo a sign change. The general position of the maximum is thus determined and central composite rotatable designs (see Cochran and Cox, p. 346, for a description of these designs) are used to specify it accurately. These designs retain the factorial points to estimate linear terms and extra points are added to determine quadratic terms descriptive of the curvature of the surface about the maximum. The equation calculated from the data is differentiated with respect to each variable and the differential equations equated to zero to numerically solve for the values of the variables at the maximum response.

Thus, the determination of relevant absorption information for atomic absorption analysis strongly suggests a study of the critical parameters of flame excitation and an assessment of the relative utility of the single-factor and the response surface experimental methods.

EXPERIMENTAL

Emission Apparatus

A Beckman monochromator (model DU) equipped with flame attachment (model 9200), photomultiplier attachment (model 4300), and recording attachment (model 92300) was the basic instrument. Integral atomizer, oxy-acetylene burners (Beckman Instruments Inc., #4030) and a 1/3 second response, 0 to 10 millivolt, Brown recorder were used in conjunction with this. The gas flow rates were controlled by a Beckman regulator calibrated with a wet-test flow meter. The vertical position of the flame region viewed was adjusted with a racking burner mount (27).

Emission Procedures

To determine the relative degrees of excitation of an element, the intensities of spectral lines were monitored using the following method. The photomuliplier sensitivity was set to the maximum, the slit to 0.010 mm. and the flame variables were adjusted to the desired levels. Then, while sample was aspirated into the flame, the dark current was adjusted to give a constant, low-level, readable background and the wavelength region was scanned automatically. The relative intensities were determined from the recorded data using the base-line technique to measure the signal above background.

Absorption Apparatus

Figure 1 presents most of the pertinent information concerning the atomic absorption apparatus and the optical arrangement thereof. Additional data required are as follows.

Light Source. Westinghouse hollow cathode lamps for holmium (WX5487), erbium (WX5486), dysprosium (WX5465) and samarium (WX4972) were used as light sources. The lamps were connected to a constant-current power supply (Lambda Electronics Corp., model 71-B) with 500-d.c. volts compliance and operated at an appropriate current between 10 and 50 milliamps. In addition, an oxyhydrogen flame consuming a 500 p.p.m. ethanol solution of europium, thulium or ytterbium was used as the light source for these elements respectively.

Detector. The multiplier phototube was used with equal dynode voltages for all stages but varied from 60 to 120 volts per stage depending on the gain required.

Photomultiplier Power Supply. The design of this unit has been described by Box and Walsh (5). The British electronic tubes specified in their design were replaced by American equivalents. The supply provides a regulated, continuously variable voltage from 400 to 1400 volts d.c. in two switch-selected ranges.

Amplifier. The metals emit strong radiation at the absorption wavelengths. To overcome this, it was necessary to modulate the light incident on the flame and tune the amplifier to the same frequency. Under these conditions, only the periodic signal was amplified thus leaving a

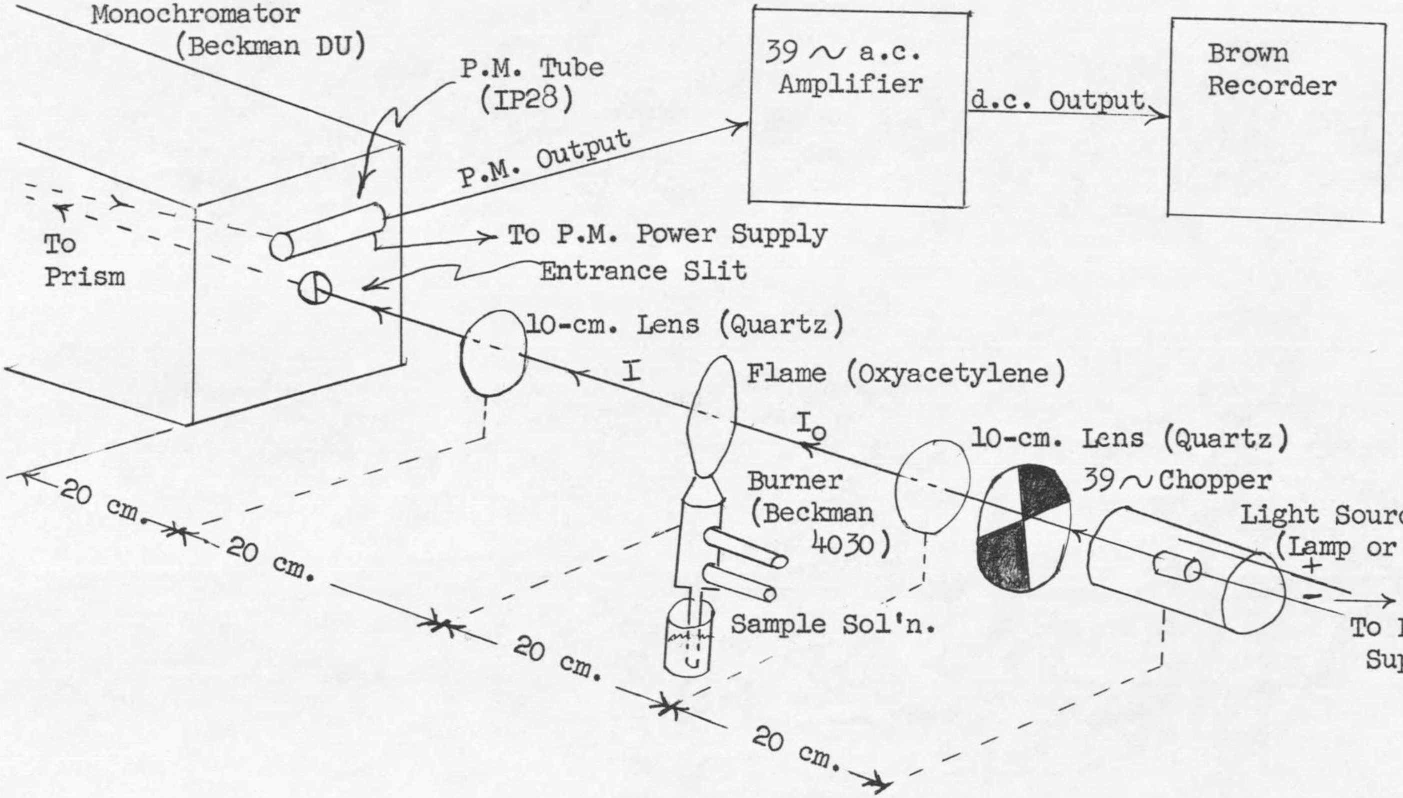


Figure 1. Atomic Absorption Appartus

negligible direct emission signal from the flame. The tuned amplifier reported by Kalmus and Sanders (21) was redesigned to accommodate our needs. The circuit, shown in Figure 2, consists of a two stage a.c. amplifier employing two parallel-T networks. One network rejects any 120 c.p.s. signal due to artificial light or full-wave rectified ripple in the amplifier power supply. The other operates as a degenerative feedback loop passing all frequencies except the signal from the light sources. The unit has a half-power bandwidth of one c.p.s. and a d.c. output for a recorder.

Absorption Procedures

Absorption measurements were made by setting the monochromator to pass only the absorption wavelength with the slit set at 0.010 mm. unless otherwise specified. The recorder was set to an arbitrary light intensity, I_o, by adjusting the photomultiplier voltage and the amplifier gain with a blank in the flame. A sample solution was then aspirated and I, the absorbed line intensity, was obtained.

Standard Solutions

Stock solutions containing 10,000 p.p.m. of the metals by weight were prepared from 99.9+% pure metal oxides (M_2O_3, American Potash and Chemical Corp.) digested in perchloric acid and dissolved as described by Fassel et al (15). These concentrated solutions were diluted to prepare standards of the desired concentrations.

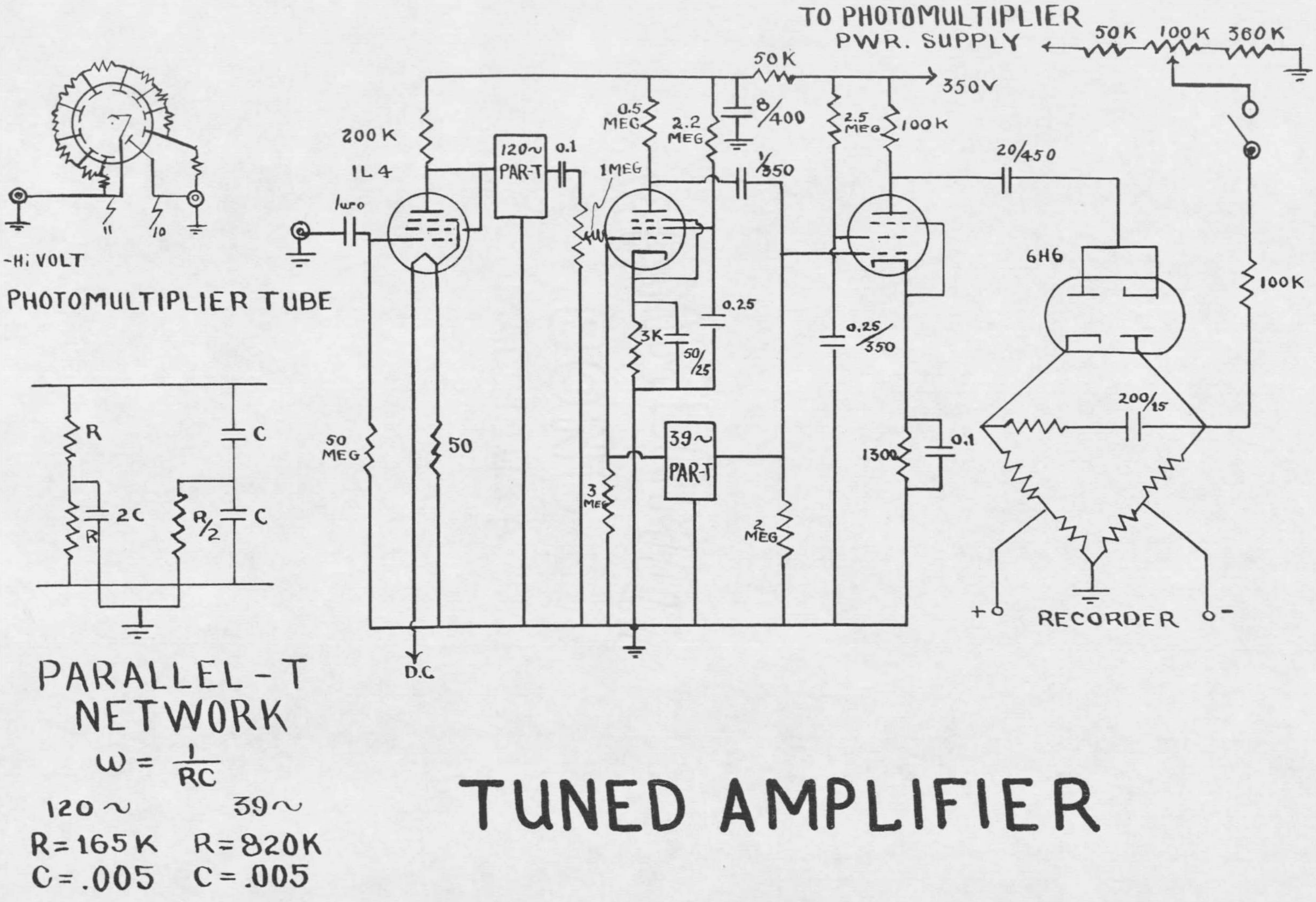

TO PHOTOMULTIPLIER
PWR. SUPPLY
50K
100K
360K
50K
350V
200K
1L4
120~
PAR-T
0.1
1MEG
0.5 MEG
2.2 MEG
8/400
1/350
2.5 MEG
100K
20/450
1μfd
6H6
100K
-Hi VOLT
11
10
PHOTOMULTIPLIER TUBE
0.25
3K
50/25
0.25/350
50 MEG
50
39~
PAR-T
3 MEG
2 MEG
1300
0.1
200/15
RECORDER
+
-
D.C.
R
C
2C
R
R/2
C
PARALLEL-T NETWORK
ω = 1/RC
120~
39~
R=165K
R=820K
C=.005
C=.005
TUNED AMPLIFIER

Figure 2

RESULTS

Solvent Choice

Various solvents, which had been reported (2,12,15,34) as producing enhancements for similar systems, were evaluated to determine their relative utility for our systems.

The conditions maximizing lanthanum emission for a series of alcohols were ascertained by the single-factor method. The relative intensities of a spectral line for equal concentrations of metal in each alcohol were determined at the conditions specified using constant instrument parameters. Sensitivity factors were calculated from these intensities using the ethanol solution intensity as a reference. The results, presented in Table I, indicate that the signals agreed within experimental error and hence, no particular advantage accrued from choosing a particular alcohol. It is of interest to note that the series of butanols with similar surface tensions, viscosities and heats of combustion, required identical flame conditions.

Table I. Optimum Excitation Conditions and Comparative Sensitivities for Lanthanum in Alcohols

	Optimum Flame Conditions			Sensitivity Factor
Alcohol	O/F	O+F (cc/min)	D (mm.)	$\frac{I\ (\text{alcohol x})}{I\ (\text{EtOH})}$
Absolute Ethanol	0.93	6000	28	1.00
Normal Butanol	0.80	6000	29	0.98
Iso-butanol	0.80	6000	29	1.00
Tertiary Butanol	0.80	6000	29	0.99
Methanol	0.75	6000	26	0.99

Similar evaluations were made for europium, thulium, and dysprosium in mixtures of ethanol and 4-methyl-2-pentanone (4M-2P) using response surface methods to specify the optimum flame conditions. This comparison was an attempt to elucidate the role of the solvent in the excitation process. Table II summarizes these results and again, no significant sensitivity increase was apparent. The data in both Tables I and II verifies that the flame conditions required are somewhat dependent on the solvent used but there is no obvious relationship between the flame parameters and such physical properties as surface tension, viscosity, or heat of combustion.

Table II. Optimum Flame Conditions and Comparative Sensitivities for Europium, Dysprosium and Thulium in Solvent Mixtures.

Metal-λ(A)	Mole Fraction EtOH	Mole Fraction 4M-2P	Optimum Flame Conditions			Sensitivity Factor I(Mix)/I(EtOH)
			O/F	O+F (cc/min)	D (mm)	
Eu4594.02	1.00	0.00	1.70	8000	15	1.00
	0.85	0.15	1.70	8000	17	1.00
	0.70	0.30	1.80	8000	17	1.01
	0.50	0.50	1.90	7600	17	1.03
	0.30	0.70	2.20	7800	17	1.12
	0.00	1.00	2.20	8000	15	1.02
Dy4045.98	1.00	0.00	1.10	8000	23	1.00
	0.75	0.25	1.10	8000	22	0.96
	0.49	0.51	1.20	7000	20	0.99
	0.24	0.76	1.20	7000	20	0.99
	0.00	1.00	1.20	6500	21	0.98
Tm4105.84	1.00	0.00	1.10	8000	24	1.00
	0.75	0.25	1.10	8000	23	1.01
	0.49	0.51	1.10	8000	22	0.99
	0.24	0.76	1.20	7500	24	1.00
	0.00	0.00	1.25	7000	24	0.97

Similar studies with ethanol-acetone mixtures were limited by the rapid deposition of carbon on the burner orifice apparently due to the presence of acetone. The low solubilities of the lanthanide-perchlorate complexes in non-polar solvents prevented evaluation of this type of sample medium. Water was not included in the investigation because of its highly endothermic effect on flames (12,17,24).

Because of its desirable aspiration characteristics, lower level of audio noise in the flame and low rate of carbon deposition, absolute ethanol was selected for subsequent studies.

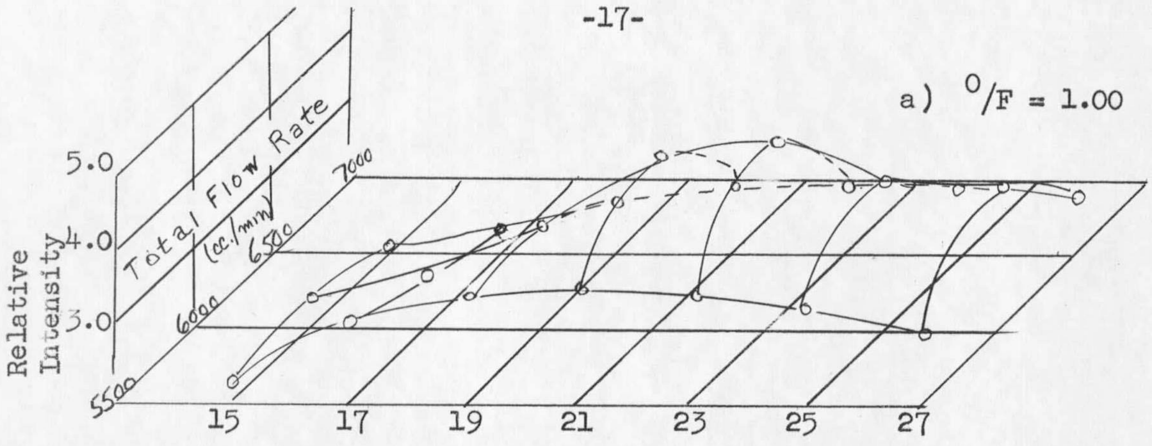
Optimum Excitation Conditions and Evaluation of Experimental Methods

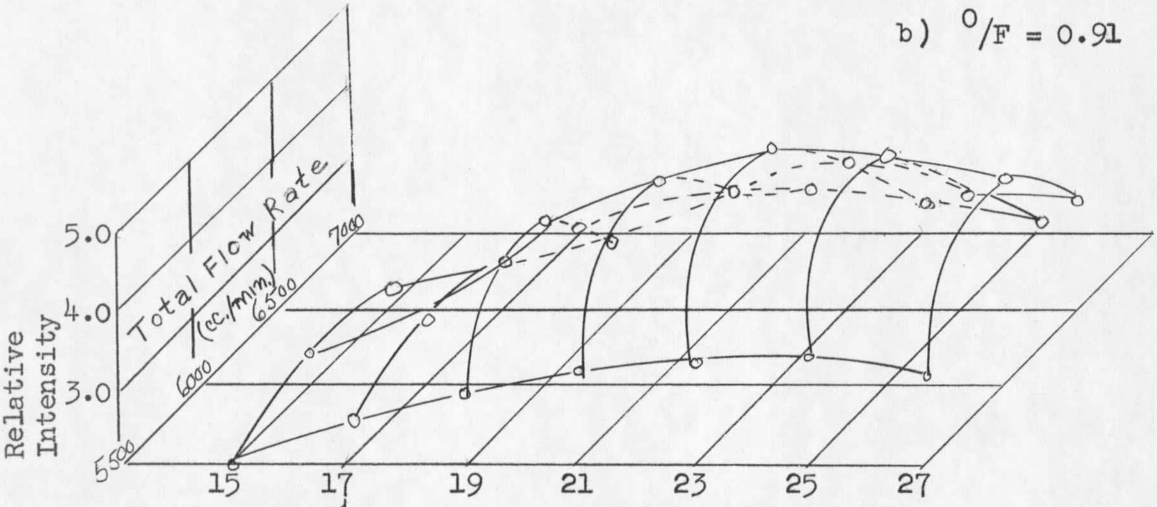
The flame conditions maximizing excitation of rare earths and the relative merits of classical (single-factor) and response surface experimentation methods were ascertained by using both methods. A comparison of the two techniques, summarized in Table III, demonstrates general disagreement between the two methods. For determining optimum sensitivity conditions, emission intensities for equal concentrations of each element were determined for various parameter combinations using constant instrument settings. The tabulated sensitivity factors were calculated using the intensities at the classical optima as references. These factors verify that the conditions specified by response surface methods produce significantly greater excitation and imply that the classical method cannot be relied upon to locate the true maxima for these systems. It was considered that a relationship between the optimum conditions and the properties of the elements might be discovered but no simple interdependence could be found with respect to properties such as: electronic configuration, excitation potential or dissociation potential of the diatomic oxides.

Table III. Optimum Flame Conditions Specified by the Classical and Response Surface Experimental Methods.

Element	Classical Results O/F	O+F(cc/m)	D(mm)	Response Surface Results O/F	O+F (cc/min)	D (mm)	Sensitivity Factor I(R-S)/I(S-F)
Lu	0.91	6000	25	1.05	7700	19	1.10
Dy	0.91	6000	26	1.10	8000	23	3.30
Sm	0.91	6000	24	0.94	6000	22	1.05
Y	0.84	6500	25	1.10	8000	22	1.10
Tb	0.84	6000	26	---	---	--	---
Nd	0.90	6000	24	---	---	--	---
Er	1.05	6000	24	1.05	8000	28	1.45
Ho	0.90	6000	21	1.10	8000	25	1.30
La	0.93	6000	28	---	---	--	---
Pr	1.00	6500	18	---	---	--	---
Tm	0.96	6000	26	1.10	8000	24	1.10
Eu	1.20	6500	18	1.70	8000	15	2.00
Yb	1.10	6500	18	---	---	--	---
Gd	0.90	6000	24	---	---	--	---

For a full comparison of the two methods and an understanding of the resultant implications, the data may be usefully considered as follows. Three-dimensional plots, constructed using the single-factor data for samarium and dysprosium are given in Figures 3 and 4. These may be taken as representative of all such plots. Comparison indicates the samarium


a) $^{O}/F = 1.00$


b) $^{O}/F = 0.91$

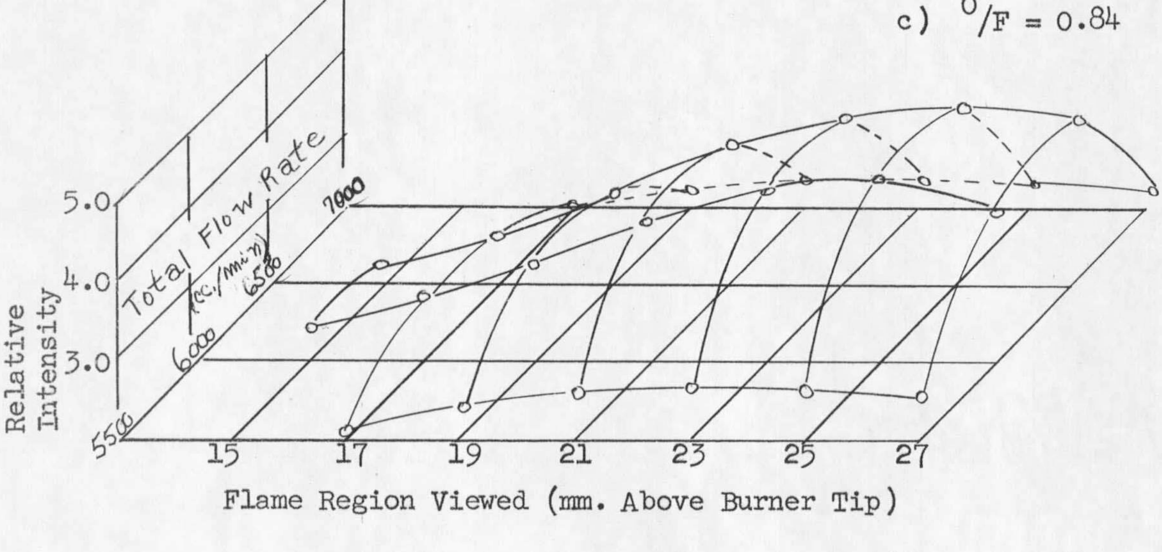

c) $^{O}/F = 0.84$

Figure 3. Single Factor Data on Samarium Emission at 441.9 mu.

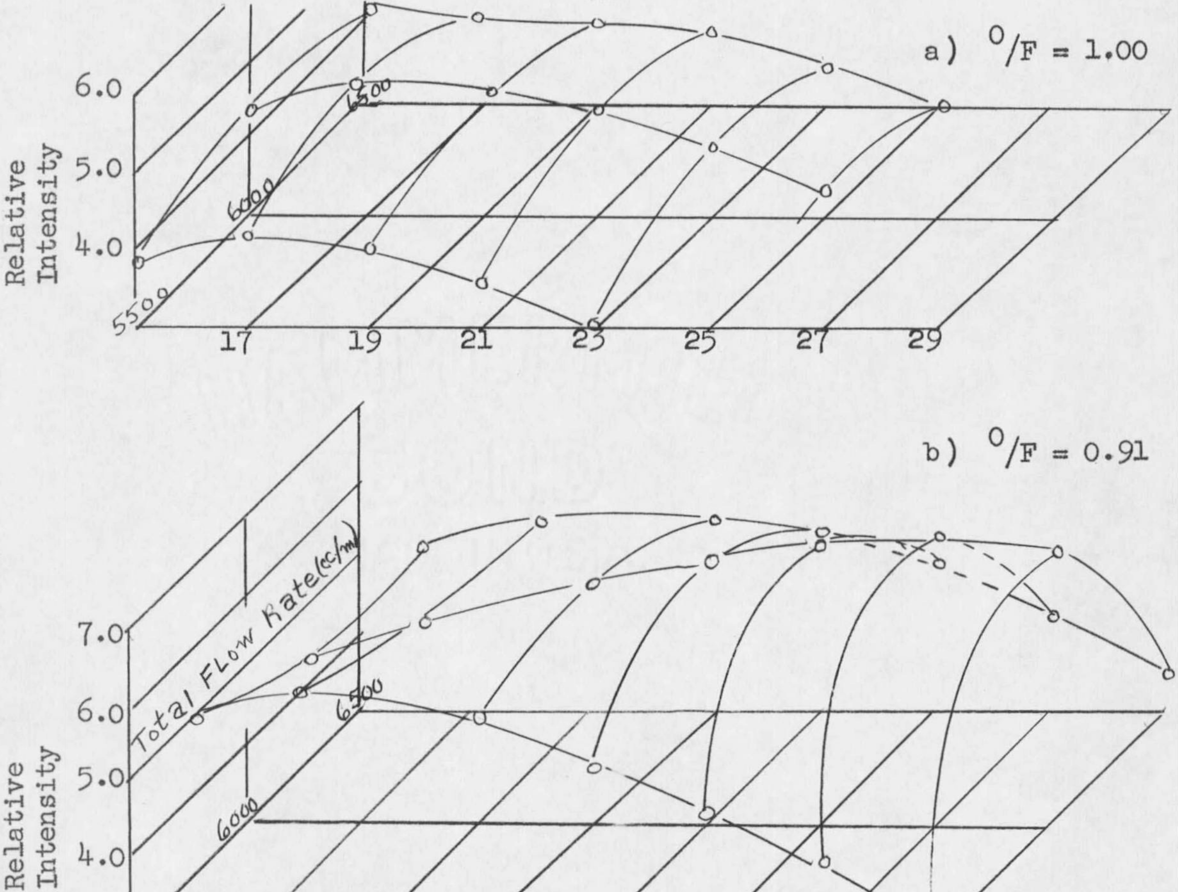


Figure 4. Single Factor Data on Dysprosium at 404.6 mu.

surface to be the simpler of the two. For samarium, the surfaces show that single-factor experimentation would produce the same results regardless of the variable levels selected to initiate the experiments. The dysprosium plots, however, suggest the possibility of other maxima.

The results obtained by application of response surface experimentation to the samarium and dysprosium systems are summarized in Tables IV and V. Arbitrary variable levels were chosen for the initial experiment in each case and the reasons for subsequent experiments are given by the calculated equations. In applying the central composite designs, the total flow rates were restricted to 6000 and 8000 cm.^{3}/min. for samarium and dysprosium respectively because of burner operation problems outside this range. The samarium results agreeably reproduce the single-factor maximum but this is not the case for dysprosium. Although the dysprosium experimentation was initiated at total flow rate levels near those specified by the classical method, the calculated equations consistently required changes to higher levels. This contradicts the existence of the troughs seen in the surfaces of Figure 4.

By converting the calculated quadratic equations to a canonical form, contour representations of the response surfaces were obtained. The samarium surface, Figure 5, illustrates a reasonably high degree of interaction between the two variables and the critical effects that these variables have on the emission intensity. Dysprosium, and the other elements investigated, all exhibited similar response surfaces. Figure 5 clearly indicates a general principle for choosing the response surface method, i.e., the effective rotation of axes due to interaction effects.

Table IV. Response Surface Methods Applied to Samarium Excitation

Experiment Number	O/F Levels X_1	O+F Levels X_2 (cc/min)	Distance Above Burner (mm) X_3	Calculated Equations
1	1.20-1.50	5000-5500	22-26	$\hat{I} = 6.27 - 2.26X_1 + 0.05X_2 - 1.33\,X_3$
2	0.95-1.15	5750-6250	9-13	$\hat{I} = 5.64 - 1.51X_1 - 0.49X_2 + 2.26X_3$
3	0.75-0.96	5600-5800	14-18	$\hat{I} = 6.00 + 1.37X_1 + 0.15X_2 - 2.69X_3$
Region of Max. $\hat{I}$	0.90-0.96	5700-6000	17-23	
Central Composite Levels	0.86-0.96	6000	17-23	$\hat{I} = 1.778 + 0.101X_1 + 0.079X_2 - 0.074X_1^2 - 0.056X_2^2 - 0.018X_1X_2$
Optimum Levels	0.94	6000	22	

$\hat{I}$ = estimated emission intensity.

Table V. Response Surface Methods Applied to Dysprosium Excitation

Experiment Number	O/F Levels X_1	O + F Levels X_2 (cc/min)	Distance Above Burner Tip (mm) X_3	Calculated Equations
1	1.25-1.30	6200-6400	15-17	$\hat{I} = 806 - 0.37X_1 + 0.55X_2 + 0.28X_3$
2	1.05-1.10	6800-7000	20-22	$\hat{I} = 8.95 - 0.29X_1 + 0.28X_2 + 0.28X_3$
3	1.15-1.20	7500-7800	24-26	$\hat{I} = 6.60 - 0.27X_1 + 0.11X_2 - 0.65X_3$
Region of Max. $\hat{I}$	1.05-1.15	>7800	21-25	
Central Composite Levels	1.05-1.15	8000	21-25	$\hat{I} = 9.101 + 0.001X_1 - 0.002X_2 - 0.072X_1^2 - 0.054X_2^2 - 0.019X_1X_2$
Optimum Levels	1.10	8000	23	

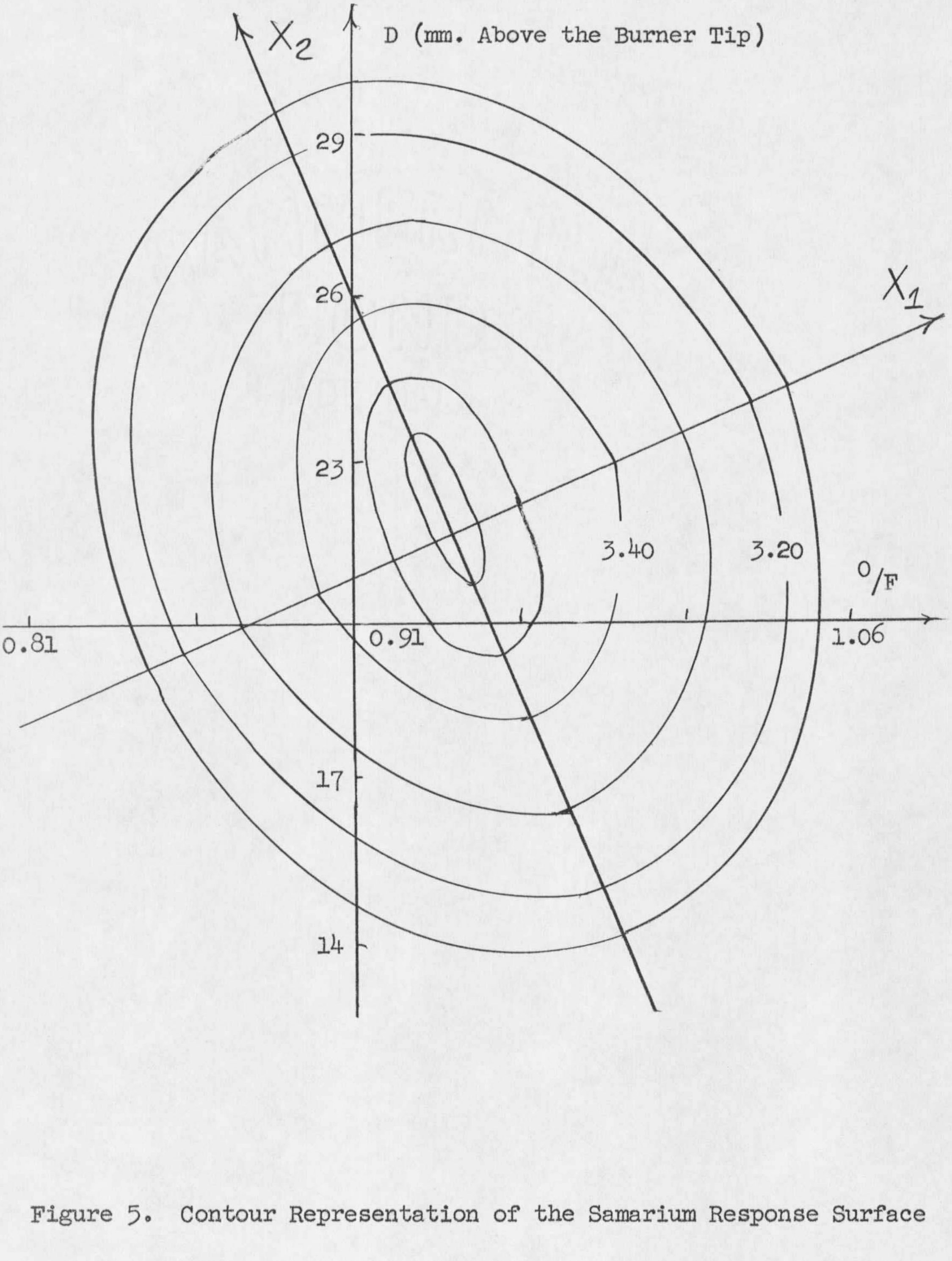


Figure 5. Contour Representation of the Samarium Response Surface

(3,4,8,11).

Absorption Wavelengths

To locate useful absorption lines, the spectrum of each source was scanned first with a blank and then with a sample in the flame. The absorbing lines exhibited intensity attenuation detected by visual comparison of the two recordings. The principle absorption wavelengths are listed with their respective analytical curves in Figures 10 through 13 (pages 31-34).

Lamp Current

Absorption is dependent on the emission characteristics of the lamp. Since these are affected by the current, it was necessary to determine optimum lamp currents. The curve in Figure 6 is typical of lamp current effects on absorption. In practice, the lowest current commensurate with a stable, measureable light output was used so that pressure broadening, Doppler broadening and self-reversal were minimized. The currents selected for use are indicated in Table VII (p. 29).

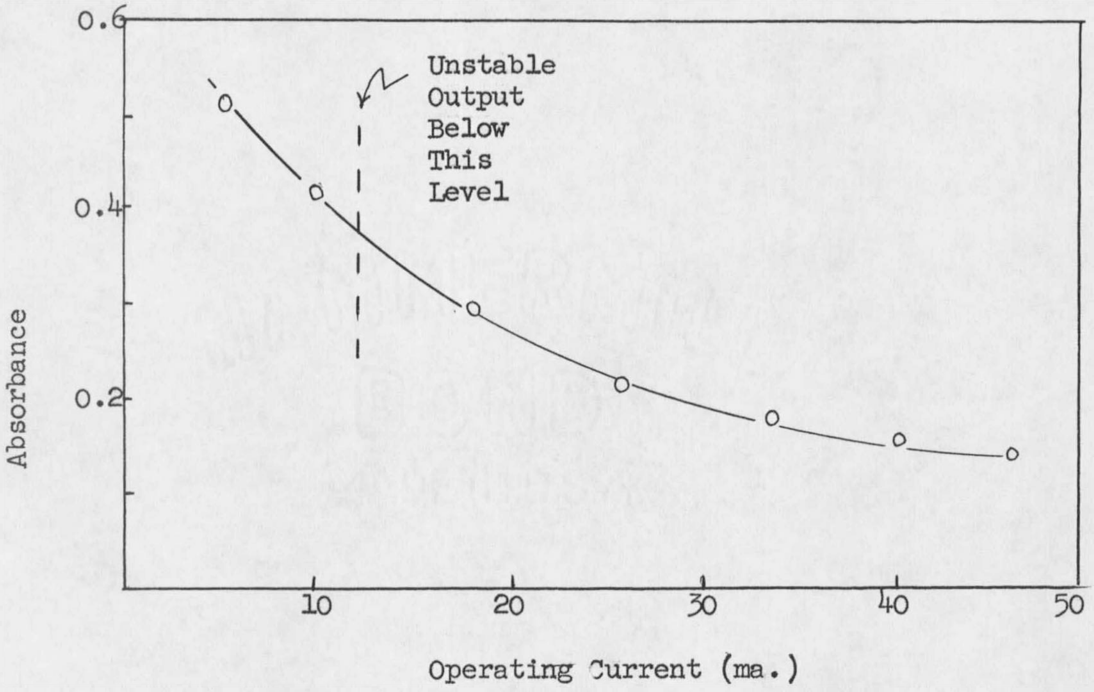


Figure 6. Effect of Lamp Current on Dysprosium Absorbance

Flames as Absorption Line Sources

Because of construction problems, rare earth hollow cathode lamps are not yet readily available from commercial sources. Consequently, auxiliary flames emitting the line spectra were investigated as possible substitute sources. Preliminary studies indicated that absorption could be observed and it was necessary to determine optimal flame parameters. Thus, the four possible combinations of oxyacetylene and oxyhydrogen flames, as source and absorbing flames, were analyzed for their effects on absorption sensitivity. In each instance, the source flame was adjusted for maximum line intensity while the absorption flame was optimized for absorption. The results obtained for europium are summarized in Table VI where the detection limits are defined as the concentration of metal in p.p.m. required to absorb five per cent of the incident light intensity. The sensitivities given are effectively the slopes of the calibration curves. The slit-widths required (see Figure 7, p.26) are indicative of the relative band-widths of the line in the two types of flame. The lower detection limits for the two cases where the fuel-rich oxyacetylene flame was used as the absorbing medium verify the increase in the neutral atom population suggested by Fassel and associates (15). The oxyhydrogen-oxyacetylene combination, as source and absorbing

Table VI. Europium Absorption Sensitivity for Various Flame Combinations

Source Flame	Absorbing Flame	Optimum Slit-width (mm)	Detection Limits (P.P.M./5%)	Sensitivity (Absorbance/p.p.m.)
oxyhydrogen	oxyacetylene	0.030	12	1.9×10^{-3}
oxyacetylene	oxyacetylene	0.020	49	4.5×10^{-4}
oxyhydrogen	oxyhydrogen	0.015	200	1.1×10^{-4}
oxyacetylene	oxyhydrogen	0.020	275	8.0×10^{-5}

flames respectively, were selected for subsequent applications because of the increased sensitivity observed with this arrangement.

Monochromator Slit-width

The narrow bandwidths of the lines emitted by the lamps permitted the selection of the minimum instrument slit-width, 0.010 mm. When a flame was used as the source, variation of the slit-width had a pronounced effect on the absorbance as seen in Figure 7. Consequently, the slit

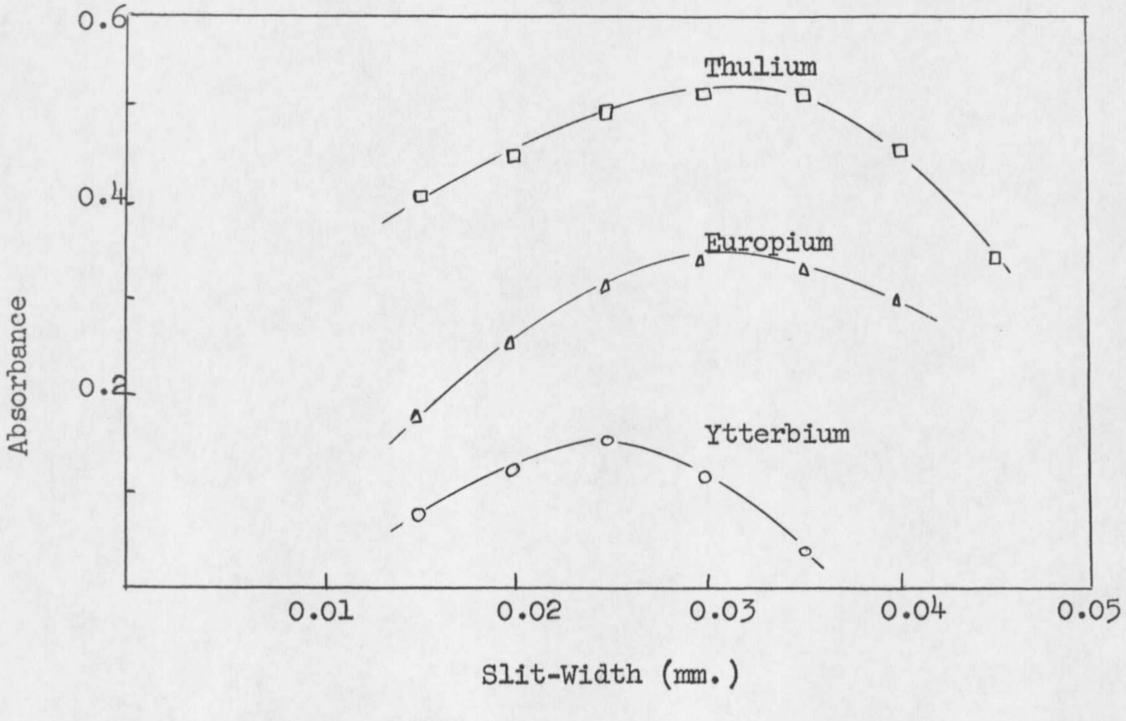


Figure 7. Effect of Slit-Width on Absorbance (Oxyhydrogen Flame as Line Source)

was adjusted to 0.030 mm. for europium and thulium and to 0.025 mm. for ytterbium for subsequent measurements.

Optimum Absorption Conditions

Response surface methods were used to specify the optimum absorption flame conditions. The neutral atom populations were found to be less dependent on the total flow rate and flame region viewed than the excited atom populations. Figure 8 demonstrates the effect of varying the flame region sampled at the optimum levels of oxygen to fuel ratio and total

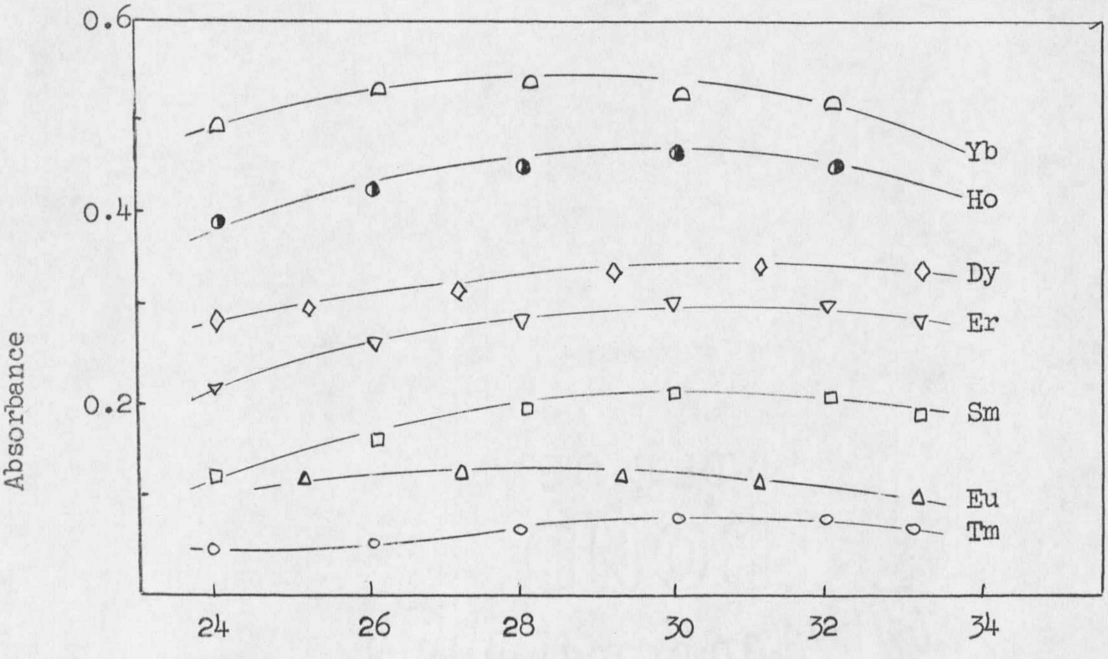


Figure 8. Effect of Flame Region Viewed on Lanthanide Absorption (At Optimum O/F and O + F Levels)

flow rate. Similar effects on the absorbance were observed when the total flow rate was varied under the same conditions. The oxygen to fuel ratio had the most significant effect as evidenced for dysprosium in Figure 9. The curves for the excited (Dy*) and unexcited (Dy^o) dysprosium populations typify the curves obtained for the other elements. The carbon population data was taken by Norrish (31), who used flash photolysis to determine the relative numbers of carbon atoms in a dry oxyacetylene flame as a function of the oxygen to fuel ratio. The carbon and the excited atom data are presented to support further discussion presented below. The flame and instrument parameters used for the elements investigated are summarized in Table VII (p. 29). In general, the flame conditions do not

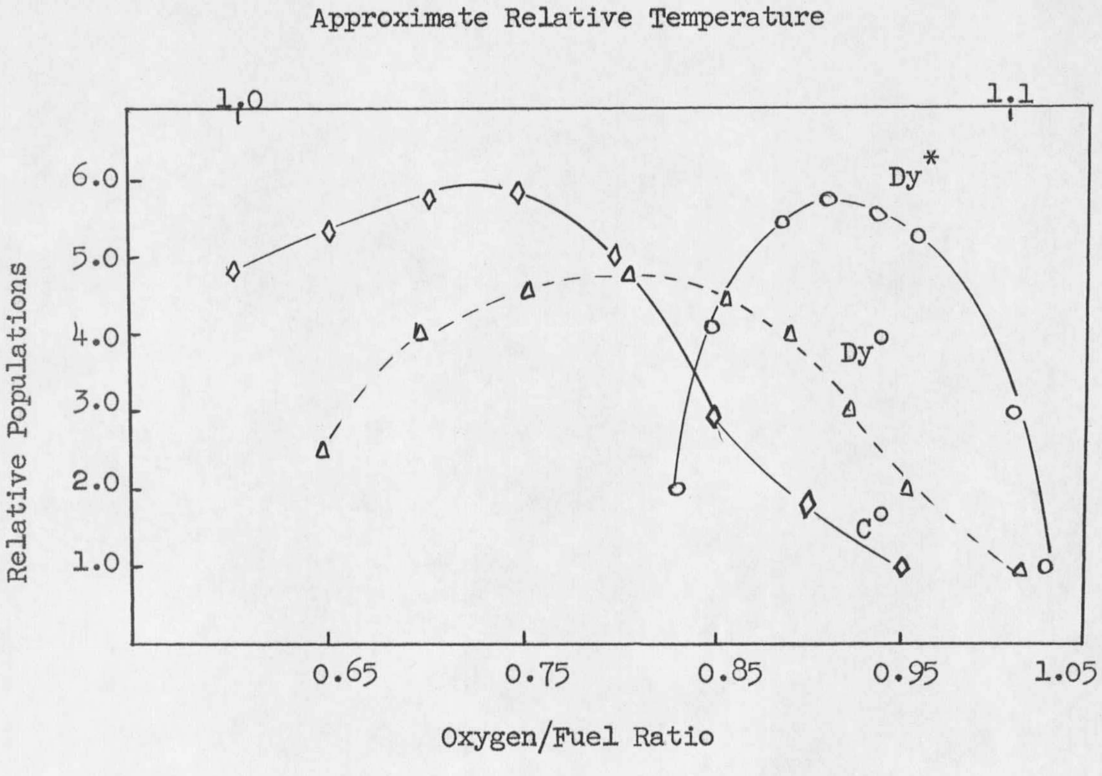


Figure 9. Effect of $^O/F$ Ratio on Dysprosium and Carbon Populations

Table VII. Flame Conditions Maximizing Absorption and Instrumental Conditions

Element	Optimum Flame Conditions O/F	O+F (cc/min)	D (mm)	Slit-width (mm)	Lamp Current (ma)	P.M. Voltage
Europium*	0.90	8000	28	0.030	--	1000
Thulium*	0.90	8000	30	0.030	--	1000
Ytterbium*	0.80	7500	28	0.025	--	1000
Dysprosium	0.80	7500	30	0.010	15	900
Erbium	0.80	7500	30	0.010	18	900
Holmium	0.75	7500	30	0.010	20	900
Samarium	0.90	8000	30	0.010	48	1000

*Oxyhydrogen flame used as line source.

agree with those required for maximum excitation. The principle differences are observed for the oxygen to fuel ratio and the flame region levels. However, reasonable agreement within the series is evident, thus supporting the previously suggested minimal temperature dependence.

Calibration Data

The absorbance, as a function of concentration, was determined for each element at its principle absorption wavelengths using the procedure and the analytical conditions previously discussed. The calibration curves shown in Figures 10 through 13 were fitted by the method of least squares. Replicate determinations were used to estimate the standard deviation for two or more points on each curve. When another flame was used as the line source, the coefficients of variation ranged from ± 2.8% to a maximum of ± 6.0%. When hollow cathode lamps were used, greater precision was obtained; a coefficient of variation of ± 3.0% being the largest observed.[4]

Detection Limits

The detection limits were conservatively defined as the concentration of metal in p.p.m. required to absorb five per cent of the incident light intensity. By reference to the point at which a calibration curve crosses this five per cent line on the calibration graphs, the detection limit for that wavelength may be obtained. In practice, it is possible to measure one per cent absorption reproducibly.

Spectral Interference

Each absorption wavelength was monitored while concentrated solu-

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[4] The samarium hollow cathode lamp used was an early design and was not particularly satisfactory. In order to obtain a stable light output, excessively high operating currents were required. As a consequence, the lines emitted were broad and did not show good absorption sensitivity. A lamp of later design, comparable to the others used, should significantly increase the sensitivity.

tions of each of the other lanthanons were aspirated into the flame. No spectral interferences were observed.

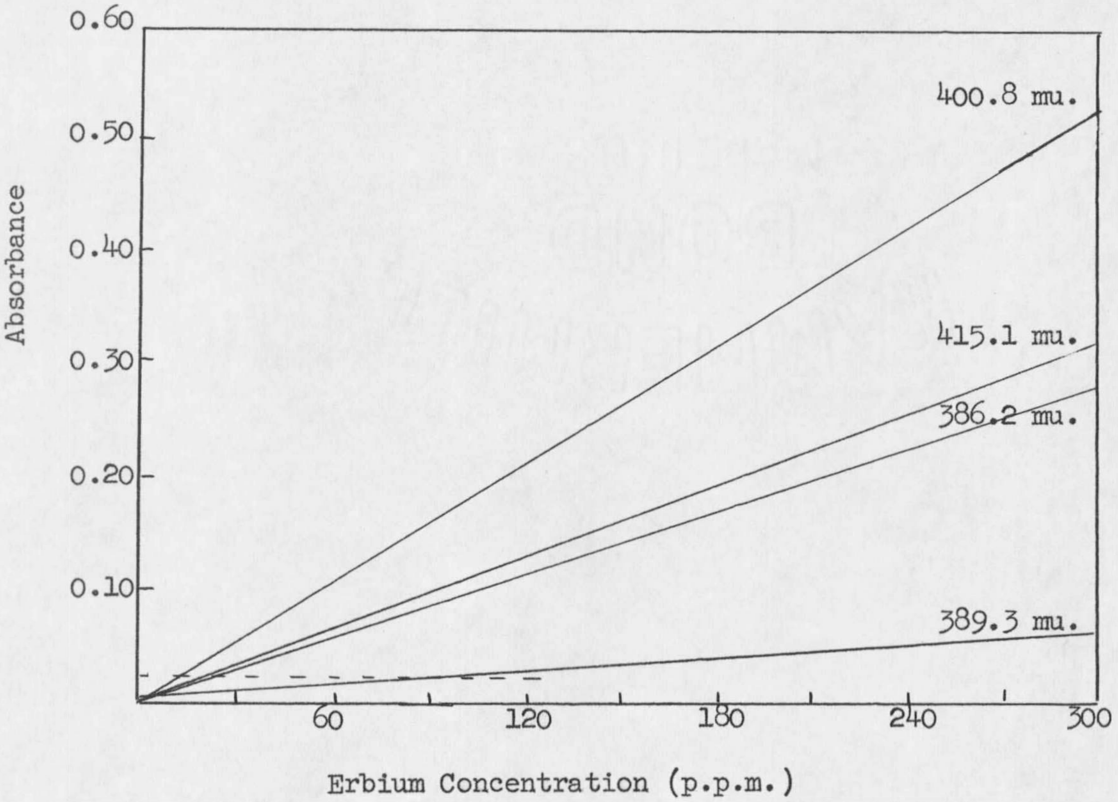

Figure 10. Calibration Curves of the Principle Absorption Wavelengths of Erbium

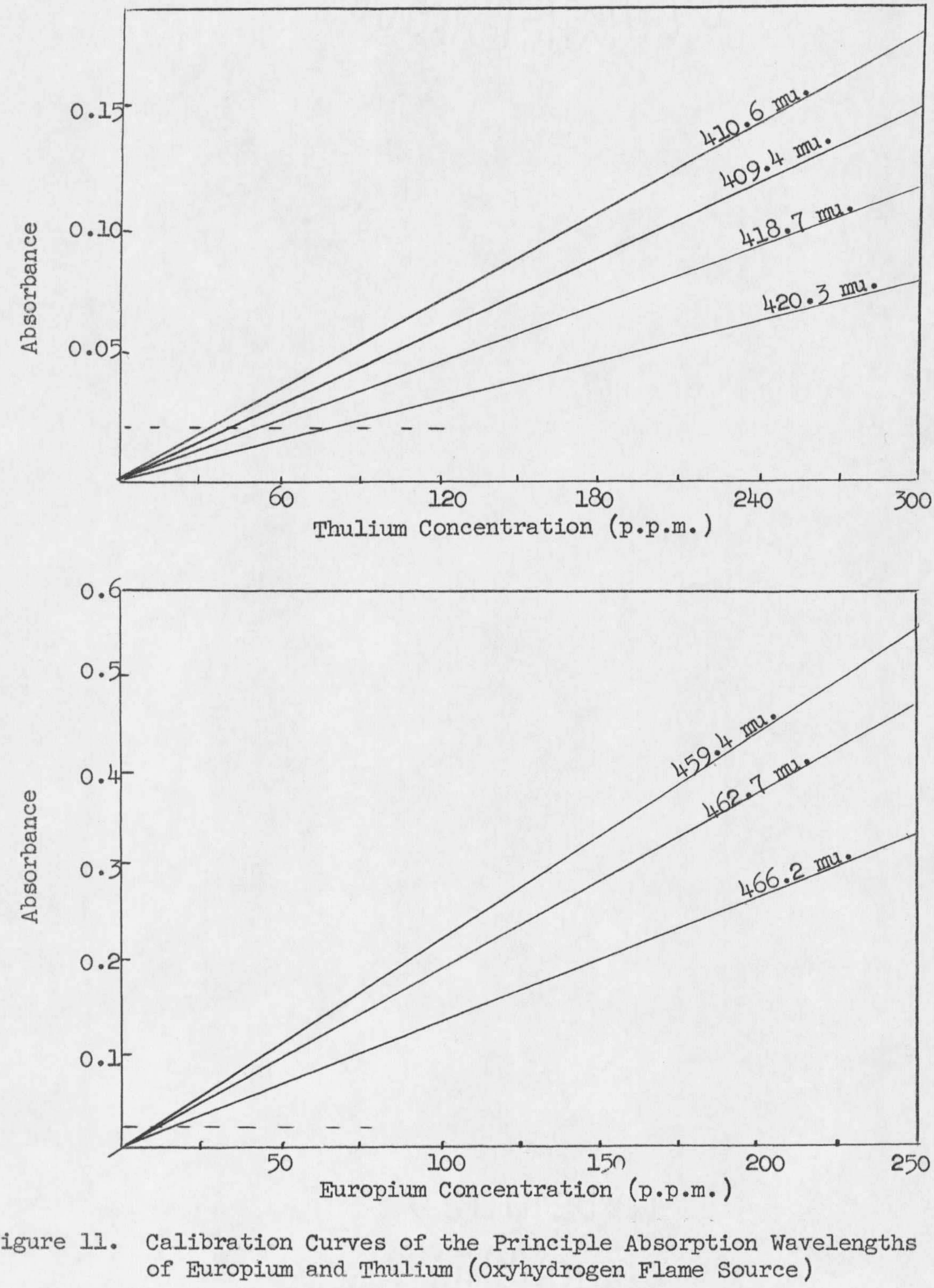

Figure 11. Calibration Curves of the Principle Absorption Wavelengths of Europium and Thulium (Oxyhydrogen Flame Source)

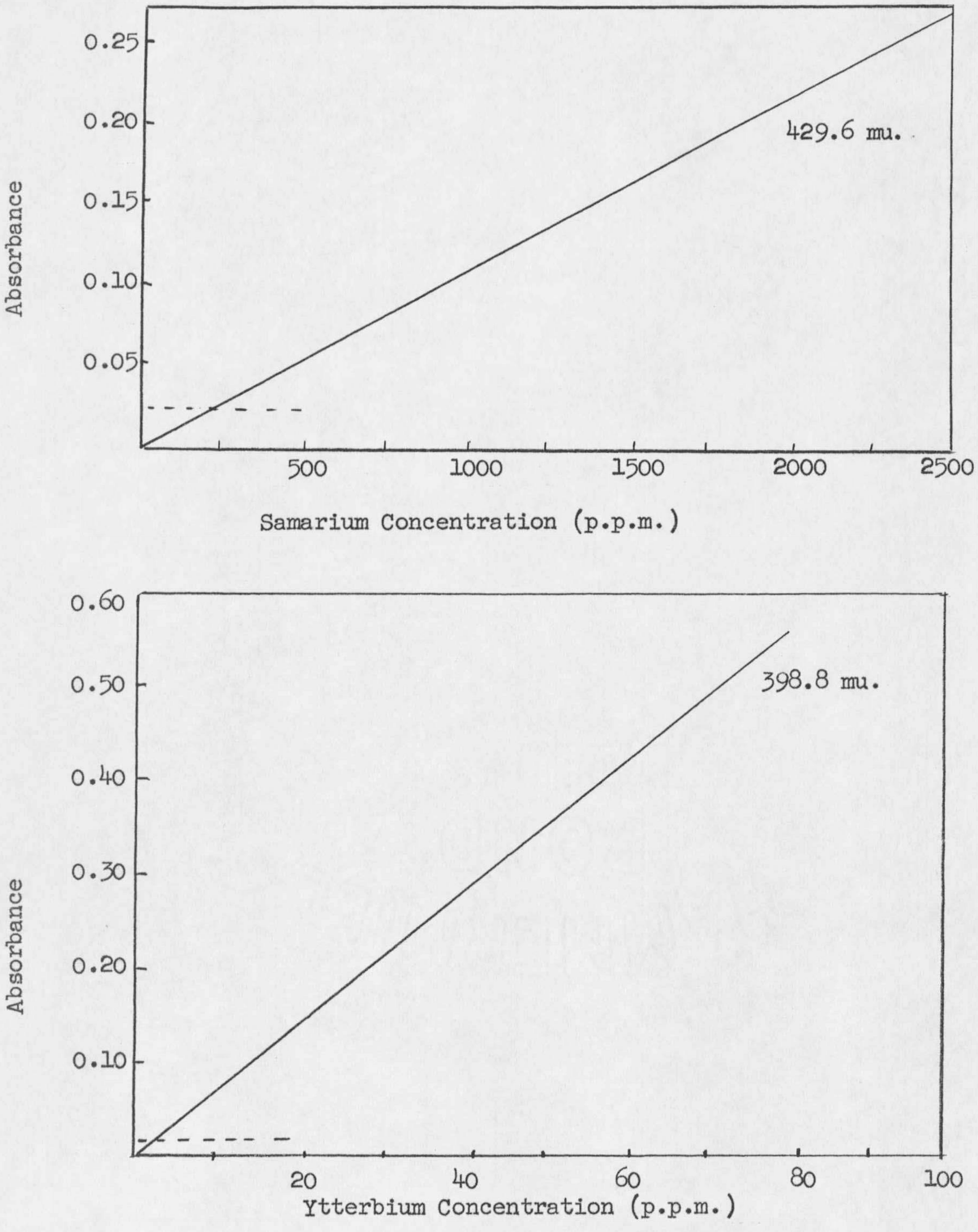

Figure 12. Calibration Curves of the Principle Absorption Wavelengths of Ytterbium and Samarium

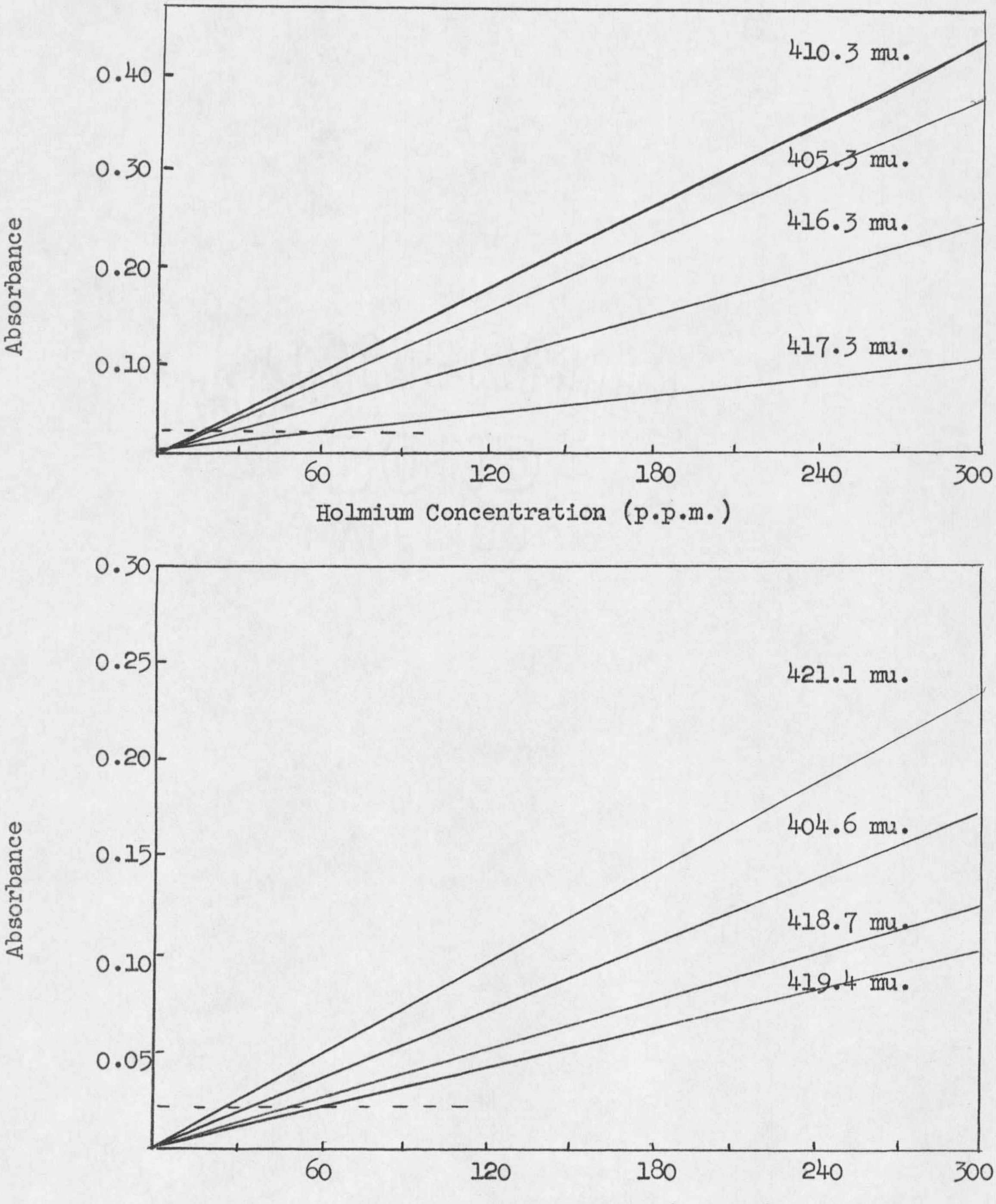

Figure 13. Calibration Curves of the Principle Absorption Wavelengths of Dysprosium and Holmium

DISCUSSION

The analytical potential of atomic absorption spectrophotometry for the determination of rare earth elements is readily evident from the results obtained in this investigation. Although not all of the members of the lanthanide series have been investigated, the data presented here, as well as the similarity of chemical properties within the series, indicate that the other members will also exhibit analytically useful atomic absorption characteristics. While the sensitivities observed were not especially good, they are comparable in magnitude to those obtained by flame photometric methods (15). These sensitivities should be significantly improved by: (1) the use of the premixing burner recently reported by Kniseley, D'Silva and Fassel (22) and (2) a multipass optical system to increase the absorption path length. Even without these proposed improvements, atomic absorption does exhibit analytical advantages over emission techniques. The lack of spectral interference from the other rare earths is certainly a significant advantage and the lower degree of temperature dependence is another. In short, these observations should encourage the adoption of atomic absorption for the determination of rare earths.

In addition to indicating analytical potential, this investigation has provided information that should be useful to theorists. The complexity of the spectra of these elements has precluded a definitive classification of these spectra (28,30,36). Thus, the absorption wavelengths reported here should provide a simple means for identifying the lines originating in the lower energy states of the neutral atom. In general, the neutral atom emission wavelengths rated highest on the intensity scale of Meggers, Corliss, and Scribner (28) coincided with the principle absorption wavelengths of the elements included in this investigation. On this basis, one can predict the absorption wavelengths of the other rare earths with reasonable certainty.

The use of a flame as an absorption line source is not novel since a similar arrangement has been used to demonstrate Kirchhoff's law (20). However, only one atomic absorption application has been reported to date (26). This is surprising since this investigation has shown that analytically useful sensitivity can be observed. Certainly the Doppler widths of the emission lines are greater for a flame than for a hollow cathode lamp so the sensitivity must be distinctly lower than that attainable with a lamp. But this technique does offer the advantage of not requiring hollow cathode lamps which are expensive, relatively short-lived, and require extended warm-up periods. The decreased sensitivity observed when oxyacetylene flames were used as the line source limited the present application to those elements that could be excited in an oxyhydrogen flame. However, many elements could be determined using the oxyhydrogen-oxyacetylene, source-absorber combination. Preliminary experiments in this laboratory have shown that sodium and calcium are readily detected at concentrations of 1 and 10 p.p.m. respectively. This order of sensitivity and the advantages offered should encourage further study of this technique.

The comparative study on the two experimental methods demonstrates that the single-factor method is less desirable than the response surface method for systems of this type. Multiple reasons may exist for the differing results obtained by the two techniques. One might suggest that they are due to application or interpretation errors. However, Fassel and associates (15) independently obtained single-factor results that agree with ours so this possibility is discounted. Rather, the inability to accurately estimate substantial interaction effects (Figure 5) when using the single-factor method (4) offers a more plausible explanation. On this basis, one could conclude that the single-factor maxima, and the implied existence of other maxima, are not real but, due to inaccurate estimation of the interdependence effects.

In summary, two principle advantages were exhibited by the response surface method as compared to the classical technique: It was more accurate and it required less total experimentation.

The failure to observe emission enhancements for different solvents is contradictory to previous investigations of this type (2,12,13,15,18, 24,34). Several complex processes occur as the organic aerosol, and its contents, pass through the flame. In essence, the aerosol must be vaporized and consumed and the metal species present must be melted, dissociated and excited; all in rapid sequence. Varying the oxygen to fuel ratio, the total flow rate, or the solvent, changes the atomization rate resulting in changes in the aerosol particle sizes and coincident deviations in the efficiency of utilization of the aerosol, the temperature, and the flame geometry. The elusive nature of the total solvent effects makes any explanatory discussion of solvent enhancements speculative. It is possible, however, that the extensive use of single-factor experimentation and the failure by many investigators to recognize the importance of the total flow rate are significant here. One might reasonably suggest that many solvent enhancements reported are not real but, rather, due to errors in the determination of the optimum flame conditions.

It has been reported (15) that the optimum flame excitation conditions are identical for the entire lanthanon series. The present investigation rather indicates that these conditions vary throughout the series. This latter situation is more reasonable if the following considerations are taken into account. It has been proposed (15) that the production of free lanthanon atoms (M^o) in the flame depends on the chemiluminescent reaction,

$$C + MO = CO + M^o \text{ (or } M^*\text{)}.$$

This reaction would be exothermic for the lanthanon monoxides (6,16), leaving the metal atoms free for excitation. Although the carbon data in Figure 9 was obtained with a dry flame (no solvent present), the close parallel between the population growths supports this suggestion as do reports on similar systems by other authors (12,19,24,34). Accordingly, the population of the flame with free atoms would depend on the dissociation potentials of the monoxides and the subsequent excitation would be subject to the excitation potentials of the spectral lines. Since both potentials may vary by several electron volts (15,28,30), it is reasonable to expect differing flame energy requirements and thus, variation in the flame parameters specified. Robinson and Kevan (35) and Buell (7) have recently presented data supporting this. In Figure 9, it can be noted that the excited atom population reaches a maximum at a higher O/F ratio than the other populations. Considering the relative temperature changes, it is evident that thermal dissociation is not the primary process in the production of neutral atoms since larger populations are observed in cooler flames. However, once the atomic species are present in the flame, the excitation process appears to be principally thermal in nature since higher temperatures are required. Hence, the excited atom population maximum occurs at an oxygen to fuel ratio commensurate with the most efficient combination of the chemiluminescent and thermal effects while the free atom maximum occurs at the level coincident with the carbon atom maximum.

SUGGESTIONS FOR FUTURE WORK

Several possibilities for investigations have been presented by this work.

(1) The potential scope of the atomic absorption technique can be widened by determining the relevant absorption information for the remaining rare earths as hollow cathode lamps become available. Certainly, the present and future absorption developments with the rare earths should also be checked for possible chemical interferences which may arise in typical analytical applications.

(2) The use of a flame as an emission line source can be extended to other elements and thoroughly investigated to determine its full analytical potential.

(3) For comparison purposes, the response surface method might be applied to an analysis of solvent effects for flame systems that have been extensively studied.

(4) Response surface methods might be used advantageously for the mathematical characterization of kinetic systems. Conventional methods for investigation of particular reaction systems usually begin with attempts to isolate the individual factors affecting the rate of reaction so that each may be studied separately. Given a priori knowledge of the factors affecting the system, they need not be isolated in order to be studied by response surface methods, i.e., all factors may be varied simultaneously. Intuitively, the result should be: better analyses of kinetic systems with less experimentation. As another alternative, the method would be useful for the optimization of reaction yields (see 3).

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