



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

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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 semiquanti-tative support for a chemiluminescent mechanism proposed by Fassel, Curry, and Khiseley (15).

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RODNEY K. SKOGERBOE

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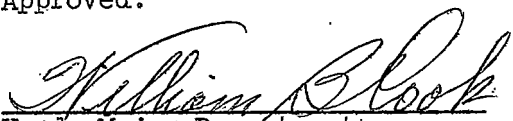
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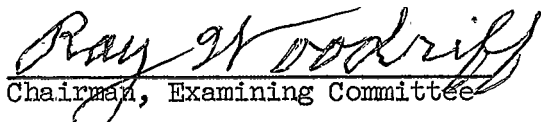
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ABSTRACT

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 lanthanons¹ 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

¹Confusion 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:

$$I_{\lambda} = I_0 e^{-K_{\lambda}l}, \quad (1)$$

where

- I_0 = 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

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

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 $\lambda \pm 0.5\lambda$, 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 chemiluminescence² 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

²A 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 experimentation³ is used to calculate linear equations relating the response

³In 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 photomultiplier 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

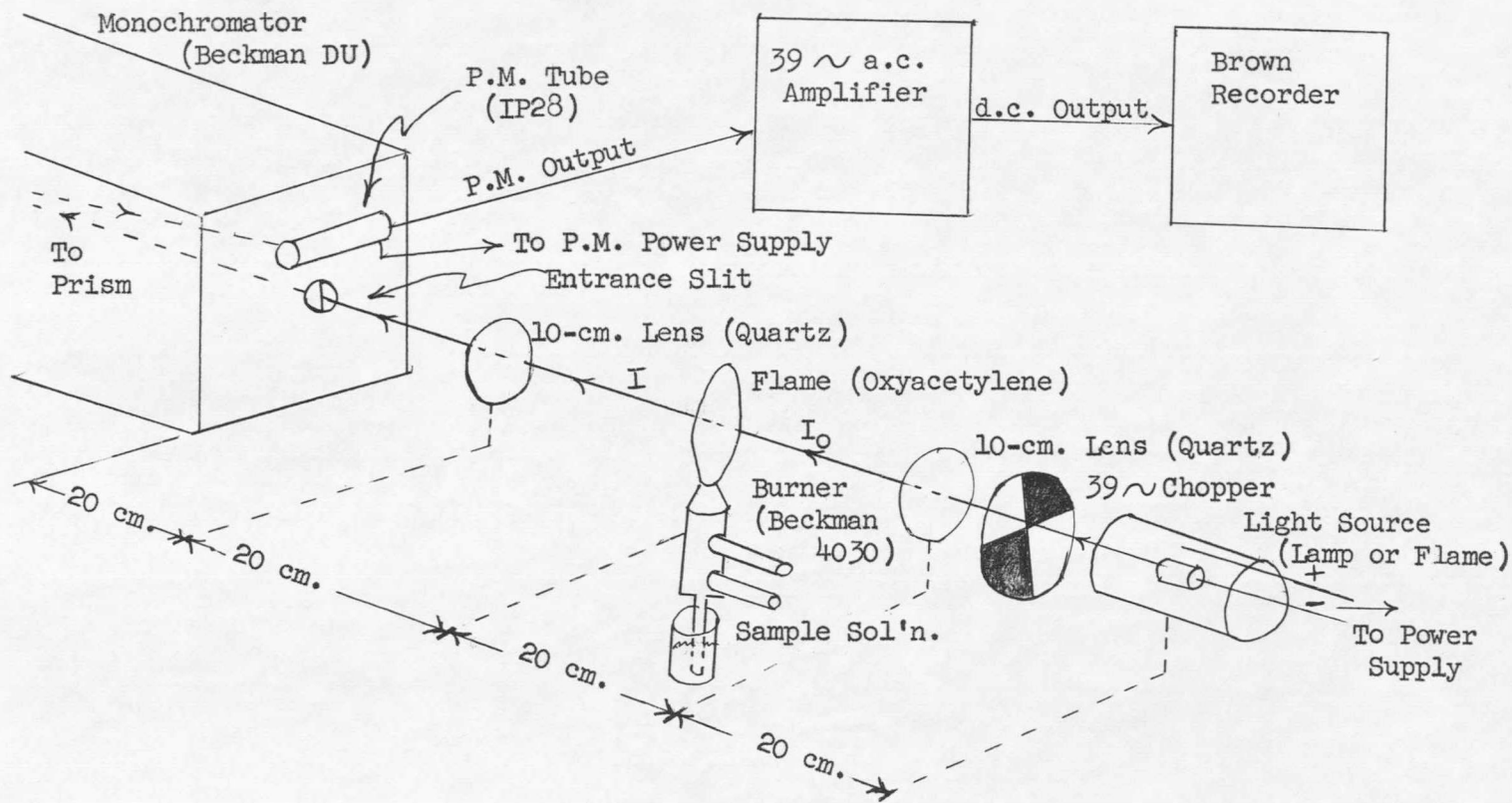


Figure 1. Atomic Absorption Apparatus

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_0 , 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.

