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Velmer Arthur Fassel
Iowa State College

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THE QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF THE RARE EARTH ELEMENTS

by

Velmer Arthur Fassel

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for the Degree of

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TABLE OF CONTENTS

I. INTRODUCTION

The great similarity in the chemical properties of the rare earths has limited the application of the familiar reactions of analytical chemistry in the analysis of this group of elements. A number of physical and physico-chemical methods have been developed and of these the spectrophotometric method has possessed the greatest general utility. In connection with the studies on the separation of the rare earths by means of the ion-exchange column technique (1, 2) the spectrophotometric method was found inadequate for some of the necessary analytical work, namely; (a) the determination of small amounts of the respective elements below the concentrations detectable by the spectrophotometric method, and (b) the determination of large amounts of those members of the group which possess no absorption bands in the region 2200-10,000 Angstroms. An investigation of other physical methods which might yield the above information led to the development of satisfactory emission spectrographic methods which are described herein.

II. ANALYTICAL ASPECTS OF THE RARE EARTHS

The various chemical, physico-chemical, and physical methods of analysis for the rare earths which have been developed have all been interrelated in the sense that they have complemented each other. The inadequacies of some of the methods have been relieved by the salient features of the other methods. Accordingly, a literature survey of all the general methods thus far proposed was made. This survey, although not exhaustive, was made detailed enough to permit an intelligent evaluation of the scope and limitations of the methods already reported and to embody those observations in the plan of procedure for devising methods which would yield the analytical information desired.

A. Chemical Methods

Because of the chemical similarity of the rare earth elements, the usual gravimetric methods of quantitative analysis have served only for the determination of total rare earths. Ordinary means of separation of the rare earths have not been at all successful and the general methods of separating the individual rare earths have been based on fractionation procedures such as fractional crystallization of various salts, fractional precipitations, fractional decompositions, and other methods dependent on differences in the basicity of the members of this group (3, 4). The application of these procedures for analytical purpose has in general been limited to the determination of percentages of certain solubility groups and for preliminary separations of the members near the extreme ends of the solubility or basicity series.

The so-called "anomolous" valencies for some of the rare earths have offered a helpful means of analysis. Cerium in the quadrivalent state is the least basic of the rare earths and this has served as the basis of a method (5, 6, 7) for the almost quantitative separation of cerium. Cerium has also been determined titrimetrically after oxidation to the quadrivalent state (8, 9, 10). The bivalent properties of europium and ytterbium have been similarly exploited. McCoy (11) found that europium could be determined quantitatively by means of the Jones reductor while Brukl (12) also has developed a titrimetric method for ytterbium. Samarium also assumes the bivalent state and praseodymium the quadrivalent state but neither has been found stable enough for quantitative estimation. It should be noted that these valence changes have also been successfully applied to the separation of europium, ytterbium and samarium from the rest of the rare earths through amalgam formation (13) and through electrolytic reduction (14, 15).

The average atomic weight method (16, 17, 18) has been found very useful in following fractionations for which comparative results have been satisfactory. Since the atomic weight of any two successive elements (with the exception of yttrium) are close together, the method has not been found very sensitive.

B. Polarographic Methods

The differences in the ease of reduction of europium and ytterbium (19, 20) from the trivalent to the bivalent state as compared to the rest of the rare earths has been exploited in the polarographic determination of these two members of the series (21, 22). The wide separation of the half-wave potential permitted a simultaneous determination of europium and ytterbium and gave results agreeing within three percent with the volumetric method. Samarium could not be determined by this method as the reduction potential to the bivalent state was found to be in the same region as the deposition of some of the other trivalent rare earth cations.

C. Magnetic Methods

One of the most outstanding physical properties of the rare earth group of elements employed for analytical purposes has been the paramagnetism exhibited by the individual members (23). Urbain (24) first recognized that the relatively large difference in the magnetic susceptibility could be utilized for following fractionations. By plotting the coefficient of magnetization of the fractions as the ordinate against the number of fractions in sequence as the abscissa, the horizontal portions of the curves were indicative of the separation of a pure rare earth (25).

This method has been found most useful for the analysis of binary mixtures (26), especially when the mixtures were composed of two constituents differing widely in susceptibility, such as europium and gadolinium, or when one of the binary constituents was one of the diamagnetic rare earths. Podashevskii and Kondoguri (27) reported an experimental error of 1 to 1.5% for the analysis of binary mixtures of neodymium oxide and praseodymium oxide and of neodymium oxide and samarium oxide. The sensitivity, however, has not been found to be as great as that of the spectrographic method.

D. X-ray Emission Spectra Methods

The characteristic X-ray spectra has been found admirably suited for the analysis of rare earth mixtures and for the determination of purity (28, 29, 30, 31). The advantages of this method were: (a) the small quantity of sample needed, (b) the preservation of the sample, (c) the simple spectra compared to the exceedingly complex optical spectra and (d) the negligible influence of the state of the substance. A sensitivity of 0.1 to 0.01% has been claimed while the experimental error has been found to be between 5 to 10% when internal standard methods were employed (32, 33, 34).

Several serious disadvantages have limited the use of this method for practical analytical purposes. The preparation of an anode or target capable of withstanding the long bombardment has often been difficult. The relatively long exposures required, especially for the purity determinations, has also been a major deterrent to the use of this method for fractionation control.

E. Fluorescent Spectra Methods

The rare earth elements predominate the short list of inorganic substances which possess fluorescence spectra, and many applications of this selective property have been made to analytical problems. This property was exhibited in solid (35, 36) and liquid solutions and in both cases has been shown to be exceedingly sensitive. Using a small pocket spectroscope and aqueous solutions, Gobrecht and Tomaschek (37) reported sensitivities of 10^{-2} molar for samarium, 10^{-3} molar for europium and dysprosium and 10^{-4} molar for terbium. Zaidel (38, 39) and coworkers have applied spectrophotographic techniques and obtained comparable sensitivities; for example, $10^{-4}\%$ of gadolinium, $10^{-7}\%$ of cerium, and $10^{-6}\%$ of terbium was detectable.

The susceptibility of fluorescence to extraneous influences, such as quenching by the presence of other ions, and the increase of intensity through stabilization by complex formation, has made this method subject to many interferences and rather large experimental errors. Zaidel (40), for instance, reported an experimental error of 30-40%.

F. Absorption Spectra Methods

Solutions of many of the rare earth compounds possess characteristic, sharply-defined absorption bands in the ultraviolet, visible, and infrared (41), and the possibility of using these absorption bands as a means of determining the respective elements in mixtures has been recognized for a considerable time. Brauner (42) and Jones (43) used the Nessler principle in determining small amounts by diluting the test solution until the absorption intensity of suitable bands appeared to be equal to those of a standard solution. A direct-vision spectroscope was used to isolate the bands. A modification of this method was also used by Friend and Hall (44). These methods were, of course, limited to the visible spectral region.

Delaunay (45) examined solutions of praseodymium and neodymium and plotted curves to show the relation between the widths of the photographed bands and the length of the absorption tube. These widths were compared with those given by solutions of unknown composition and on the assumption that Beer's law was obeyed, the concentration of the solutions giving bands of equal widths were taken as inversely proportional to the length of the absorption tube. A weakness of this method was the diffuseness of many bands in the dilute solutions.

Yntema (46) employed another method based on finding the dilution necessary to effect the disappearance of the most persistent band of a given rare earth in a mixture under rigid photographic conditions. Inoue (47) found that cerium could be estimated quite accurately in this manner.

Muthmann and Stutzel (48), using a spectrophotometer, increased the sensitivity by isolating the wavelength regions of the absorption maxima. The advent of commercial moderately priced photoelectric spectrophotometers for use in both the visible and ultraviolet greatly accelerated the application of this method. Rodden (49) has investigated the spectrophotometric determination of praseodymium, neodymium, samarium, dysprosium, holmium, erbium, thulium, and ytterbium, and this method has been extensively used in this laboratory for following the ion-exchange resin-column fractionations (1, 2).

With the exception of the limitations to be discussed later, this method has been found to be superior in accuracy, simplicity of operations, rapidity, and general application. Particularly, the feature that none of the frequently small and rare samples were lost during the analyses has been a very desirable characteristic of this method.

The fact that lanthanum, yttrium, terbium, and lutecium show no appreciable absorption bands in the wavelength regions covered by ordinary spectrophotometric apparatus has made it impossible to determine these four members by spectrophotometric measurements. Coincidence and overlapping of absorption bands of some of the rare earths has also limited the use of this method for the analysis of some mixtures.

A limitation in the application of the spectrophotometric method in purity determination of the rare earths has been the lack of adequate sensitivity. For example, the limits for determining samarium in purified neodymium and europium in purified samarium have been found to be approximately 1 and 4 percent respectively (50).

G. Emission Spectra Methods

Many statements in the rare earth literature indicate that the purity of rare earth preparations was verified by the investigation of the optical emission spectra. Apparently most of these analyses were made on a qualitative or semiquantitative basis, for the literature on quantitative applications to the rare earths has been meager.

Selwood (51) investigated the semiquantitative determination of a number of rare earth and non-rare earth impurities in neodymium and yttrium. No quantitative data was presented and apparently the estimations were correct only to within a factor of ten.

The studies by Bauer (52) on the use of the arc spectrum for the quantitative analysis of difficultly vaporized substances included an investigation of the determination of lanthanum oxide in synthetic mixtures of aluminum oxide, calcium oxide, and iron oxide by using zirconium oxide as internal standard.

An experimental error of ±10% was reported. The unusual mixtures employed by Bauer restricted his method mostly to academic interests.

Hopkins (53) and his coworkers investigated the determination of some individual rare earths in complex mixtures. They developed three methods which differed in the choice of internal standard and technique. The analytical results obtained on twenty rare earth mixtures by the use of these three methods did not, however, show satisfactory agreement. Quoting from the paper:

> The differences in the results obtained were undoubtedly due to such variations as the unequal dispersion at the wavelength of the line pairs used in the various determinations, the choice of the different internal standards, and the determination of the base line, as well as the inevitable errors introduced by the inconstancy of the arc and the various factors which influence the intensity of lines upon the plate. . . . The variations in the triplicate analyses are too large for a successful analytical method. But it must be borne in mind that there are no methods for complete analysis of rare earth ores and that the problem presents a good many serious difficulties. The author's work has progressed far enough to convince them that these difficulties are not entirely insurmountable and that further refinements will develop a method by which the composition of the unfractionated extracts of rare earth ores may be made with a reasonable degree of accuracy.

Gatterer and Junkes (54) have reported a quantitative method for the determination of europium in samarium and gadolinium possessing an experimental error of ±5%. The method proposed was exceedingly laborious, since nine separate excitations were made for each sample in order to favor a statistical reduction of the overall experimental error.

Lopez de Azcona (55) has determined the relative strength of lines of a number of rare earths when combined with a base mixture of mercuric oxide or sodium chloride and developed a method for the determination of gadolinium and samarium for which an accuracy of ±3% was claimed. The College Library was still trying to locate a copy of this journal at the time this paper was written. The abstract in Chemical Abstracts did not include any details of the method.

A method of visual spectrographic analysis based on the excitation of the molecular spectra has been used by Piccardi (56). The earth oxides were excited in a special gas flame. This method was used in particular for the approximate analyses of those rare earths which possessed no characteristic absorption spectra.

H. Selection of Method for Further Study

The choice of the method or technique for further study was conditioned primarily by the features which were considered to be desirable for the methods which were to be developed. These were:

(a) The methods should be capable of yielding the analytical information stated in Part I (Introduction).

(b) The method should be of general application; i.e., a procedure developed for the determination of small amounts of samarium in neodymium should with minor changes in the measurement of the physical or chemical property be adaptable for the determination of, say, europium in samarium.

(c) The methods should preferably have an experimental error of ±5% or less.

(d) The time requirements per analysis should be reasonable.

(e) Only a small amount of sample should be required.

A survey of the various methods discussed above indicated that only the X-ray, fluorescent, and emission spectra methods possessed a fair compromise of the desirable features. Even though the emission spectra methods reported in the literature were not satisfactory either from the standpoint of large experimental errors or of time consuming operations, this approach merited further study. The many recent advances of technique and instrumentation in emission spectroscopy especially favored this choice.

During the last two decades quantitative spectrographic analysis has abundantly proven its value for the determination of small amounts of impurities, but its application to the quantitative determination of major constituents has experienced limited study and success. This has been due primarily to the fact that the experimental errors of spectrographic methods have remained constant, regardless of the concentrations involved. Accordingly, chemical methods have far surpassed spectrographic methods in accuracy for analyses involving the determination of major constituents. The limited scope of application of chemical methods for the analysis of rare earths has however favored other physical methods of analysis. A study of the possibility of extending the scope of the spectrographic method to include the quantitative determination of major rare earth constituents was therefore also undertaken.

III. QUANTITATIVE ANALYSIS BY MEANS OF EMISSION SPECTRA

A. Theoretical

If an atom is in some way activated by thermal, radiant, or electrical energy, the various electrons are pushed into the outer higher energy levels of the atom by the excitation force and the potential energy of the atom is thereby increased. The return of the excited electrons to the lower energy levels results in the emission of radiant energy or light whose wavelength is determined by the energy difference of the two electronic states between which the transition took place. This energy difference may be indicated by the equation

$$E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

where E_2 = energy of the atom in higher energy state
E_1 = energy of the atom in lower energy state
h = Planck's constant
ν = frequency of the light emitted
c = velocity of light
λ = wavelength of the light

The dispersion of this light by a spectrograph produces a spectrum which is characteristic of the atom. Modern theoretical and experimental study of spectra has shown that the characteristic lines due to an element, which seem to be scattered haphazardly, are actually distributed according to fixed and well defined laws. The electrons which have been excited can only be forced to certain predetermined energy levels and can return to their normal positions only through a certain number of finite transitions. The many possible values of these energy levels and energy changes are characteristic of the atom and since each value of the energy change corresponds to emitted light of a definite wavelength, the observed distribution of these wavelengths must also be characteristic of the atom. This is the basis of qualitative spectrographic analysis.

B. Historical

The early use of spectroscopic methods in the qualitative identification of elements naturally led to consideration of quantitative determinations. The development of methods of estimating the quantity of a given element present date from 1874 when Lockyer (57) noted that the length of spark lines at each electrode varied with the concentration of the material in the spark source. Hartley's (58) work on the persistent lines or "raies ultimes" laid the basis of an approximate quantitative spectrographic analysis and indicated the correlation between element concentration and line intensity. Pollok and Leonard (59) continued Hartley's investigation and published a series of papers on the principle lines of elements in the spark spectra. De Gramont published a long series of papers during the period 1907 to 1920 most of which dealt with the persistent lines and their application to spectrum analysis (60). De Gramont also first proposed the use of standards photographed on the same plate for visual comparison of relative strength of the spectral lines. In spite of de Gramont's demonstration of the value of spectral analysis for quantitative analysis, the methods were disregarded until Meggers, Kiess and Stimson (61) published a number of methods for the analysis of nearly pure metals. Their work also marked the beginning of spectrographic analysis in the western hemisphere. Following this revival, spectrographic analysis experienced an almost astronomical growth during the next two decades. This came as a result of developments which increased the accuracy of the method. The foremost of these advances were: (a) the perfection of photometric devices for measuring photographic line intensity, (b) the fundamental work by Gerlach and coworkers (62, 63, 64) on the development of internal standard control of the excitation and photographic variables, and (c) the development of radiation sources capable of producing more reproducible excitation.

This rapid growth was to a large extent empirical and accordingly the literature has been abundantly filled with references to a large array of different excitation sources and methods of analysis. Many of these have merely been modifications in technique and method. Harrison (65) has pointed out that the fundamental basic method may be broken up into the following widely different but still closely related steps:

(1) Preparation of the sample
(2) Excitation of the spectrum
(3) Dispersion of emitted radiation by the spectrograph
(4) Photography of the spectrum
(5) Determination of intensity of the spectrum lines and correlation with concentration.

That so many different combinations of the chemical, physical, optical, and electrical variables in the above steps have been used has been a clear indication that there is no universal method satisfactory for all problems. Considerations of form, type and amount of sample, sensitivity, and accuracy required have compelled studies on all the variables to determine the most satisfactory conditions.

It was not within the scope of this paper to discuss even superficially the many methods that have been proposed. However, a discussion designed to acquaint the reader with the basic techniques, methods, and apparatus used in the experimental portion seemed appropriate (66).

C. Spectrographic Light Sources

The selection of a suitable excitation source is usually the first step in attacking the development of a new analysis. The ideal source would be one in which the spectral lines of each element in the electrodes or the discharge varied in intensity with concentration according to some simple law (67). Unfortunately no light source fulfilling these qualifications has been developed.

The spectral sources that are employed are usually those which perform the function of vaporizing and exciting the particular samples in the most accurate and reproducible manner. This has naturally led to a diversity of light sources. Most of these, however, can be grouped into 3 main classes: (a) flames, (b) arcs, and (c) sparks, which are related in the sense that, for each source, thermal excitation is the predominating factor in the production of the spectra (68, 69, 70).

1. Flames

Although flames are the classical sources for spectrographic analysis, their scope of application is limited to about 25 elements whose spectra are excited by the relatively low flame temperatures. The most successful method of flame analysis is that of Lundegardh (71) in which the sample in aqueous solution is atomized into an airacetylene or oxyacetylene flame.

2. Direct current arc

The electric arc, because of its high sensitivity and versatility of application, is the most widely used source. It requires only a d-c power supply having an open current voltage of at least 200 volts, a regulating resistance and electrodes for the sample. The sample electrodes are generally metal self electrodes or graphite electrodes which contain the sample in a cavity. The d-c arc yields higher sensitivity of detection than most of the other sources for the majority of the elements and is the most readily adaptable to different types of material (72). For the analysis of refractory oxides, geochemical specimens, and inorganic chemicals it offers the best means of excitation.

The general usefulness of the d-c arc for accurate quantitative analysis is impaired, however, by the erraticness and poor reproducibility of the arc discharge. A more detailed discussion of the arc discharge and how its objectionable variabilities may be reduced will be found in the experimental section of this paper (Part IV C).

3. Alternating current arc

This source, first introduced by Duffendack and Thomson (73), is designed to overcome the unstable characteristics of the d-c arc but still retain adequate sensitivity. It consists essentially of a 2000 to 4000-volt transformer equipped with a variable reactance or variable resistance, or both, to regulate the output current to 2 to 4 amperes across an analytical gap of 1 mm or less. The voltage is sufficient to produce on each cycle an ionizing spark which is followed by an arc until the gap voltage falls too low to maintain the discharge. The resulting discharge is much more reliable than the simple d-c arc.

This source has been applied to the analysis of caustic liquors (74), biological analysis (73), and organic and heavy chemicals (75). In all these cases the arc was maintained between two graphite or metallic electrodes upon which the sample solution had been evaporated.

4. Alternating current spark

Spark excitation is predominantly used for the analysis of metals in which the metal serves as its own electrode. A spark source operates from a transformer or other high-voltage supply of 10,000 to 50,000 volts which charges a suitable condenser. The condenser then discharges through a spark circuit containing conductance, resistance, and the analytical gap.

In ordinary spark sources the charging voltage of the condenser equals the breakdown voltage of the analytical gap, the latter being nearly uncontrollable after the first sequence of sparks. In order to make the discharging voltage of the condenser independent of the conditions in the analytical gap, a synchronous-motor-driven (76, 77, 78) or electronic (79) interrupter is placed in the spark circuit and by adjusting the phase angle only a definite portion of the spark phase of the discharge excites the sample. In this manner a highly-reproducible controlled type of spark excitation is obtained.

The very nature of the controlled spark excitation is conducive to greater accuracy and reproducibility. The accuracy is high because: (a) since each spark is controlled, the total exposure is a summation of discharges of equal excitation properties, (b) many hundred portions of the sample are excited by the large number of individual discharges, (c) erratic and differential volatilization is eliminated, and (d) the influence of one element on another is small because the concentration of material in the discharge is low compared to the large amount of energy available (80).

The chief limitations of the spark lie in its low sensitivity as compared to the direct current or alternating current arc and the difficulties encountered in the analysis of powders and solutions.

5. Miscellaneous sources

Besides the conventional sources discussed above, there are many others (81). Many of these are merely variations and modifications of the conventional sources.

A recent addition to this list of sources worthy of mention is a highly-flexible, all-purpose unit capable of producing reproducible discharges representing an almost continuous graduation from arc-like to spark-like excitation (82, 83).

D. Internal Standard Method

Early methods of quantitative spectrographic analysis were based on various modifications of the general procedure of estimating the concentration of an element by visual or photometric comparison of line intensity with a series of standard spectra in which the element was varied over a known range. This comparison or external standard method has been found adequate for many analytical applications, and in some special cases the absolute reproducibility of intensities has been such that this method has approached in accuracy the more refined internal standard method which will be discussed subsequently. For most applications, however, absolute relative intensity measurements have not possessed the desired reproducibility for quantitative work. Gerlach and Schweitzer (64) recognized that most of the intensity variations were associated with fluctuations in the spectrographic source and proposed the method of internal control. This method was based on the comparison of the intensity of a reference line of the principal or basic element in the material to be analysed with the line of the element to be determined. As originally proposed, selected line pairs were so chosen as to exhibit equal intensities for a number of concentrations in the range for which the analyses were made. The analyses then consisted of observing which of the pairs showed equality in intensity of the photographed spectrum of the unknown sample. After the introduction of the microphotometer, this method was further refined so that only one line pair was used and the ratios of the intensities of the pair was correlated with concentration. Nitchie and Standen (84) extended the method by adding to the sample a selected constant amount of an element not originally present, this element then serving as the internal standard.

In the internal standard method the line radiation of the element to be determined and the comparison internal standard element arose simultaneously from the same light source. In order to fully exploit this internal control on the excitation variables, Gerlach further proposed the use of a "homologous pair" of lines. These were lines whose intensities were affected in the same manner by variations in the arc or spark conditions in the analytical discharge.

The choice of a "homologous pair" for a particular analysis was made by studying the effect of varied conditions of the arc or spark, such as changes of voltage, current or inductance, on the intensity ratio. A theoretical approach to the selection of a line pair was also helpful. This included considerations of excitation potential, susceptibility to self absorption, and nature of the spectral terms between which the transition took place to produce the lines. For example, Foster and Horton (85) used the boron line at 2497.7 Å which arises as $^2S_{1/2} \longrightarrow {}^2P_{1/2}$ and for internal standard the gold line at 2427.9 Å which arises as $^2P_{1/2} \longrightarrow {}^2S_{1/2}$. Both were arc lines and both ended in the ground term. Since the latter characteristic made both lines subject to self reversal, a spark discharge was used to reduce the reversal effect.

A perusal of the literature reveals that in many applications of the internal standard control no attention is paid to atomic origins and parallel behavior in excitation and volatilization properties. In those cases the internal standard serves only in fixing the general intensity level and corrects only for such variations as optical misalignment, exposure time, photographic plate characteristics and developing conditions. It should be noted that at best internal standard control tends to correct for variables other than concentration but the correction is not precisely accurate. A statistical study by Vincent and Sawyer (86) showed that the greatest error of spectrographic analysis is still to be found in the excitation phase. Therefore, for maximum accuracy, an attempt is made to reduce all variables to a minimum and to apply internal standard control to correct for the residual variables still remaining.

E. Spectral Photometry

In quantitative spectrographic analysis the intensity of the radiation in a spectral line or the ratio of intensities in a selected line pair is correlated with the concentration of the element in the spectral source. The photographic plate is the most widely used medium for the measurement of radiant energy, although recent developments in the direct photoelectric measurement (87, 88, 89, 90) of spectral line intensity may supercede photography to some extent in the future. When photography of the spectrum is employed it is necessary to determine intensities from the blackening of the photographed image. To accomplish this with the accuracy required for quantitative analysis the best available techniques of photographic photometry (91) and a full understanding of the photographic processes are needed (92).

The quantitative determination of spectral line intensity from the spectrograms involves the measurement of the density of the photographed image. These photometric measurements are made with some form of microphotometer (93), which measures the amount of light transmitted through the silver deposit of the image. Photographic density, $\underline{D}$, is computed from these measurements by the equation $D = \log I_0/I$, where $\underline{I_0}$ and $\underline{I}$, respectively, are the intensities of light transmitted through a clear, unexposed portion of the plate and through the image formed by the spectral line.

It is unfortunate, however, that density is not a linear function of intensity. The relationship between the two is most conveniently expressed by the H and D curve, also called the characteristic and D/log I curve, which is a plot of density versus log relative intensity (Figure 1).

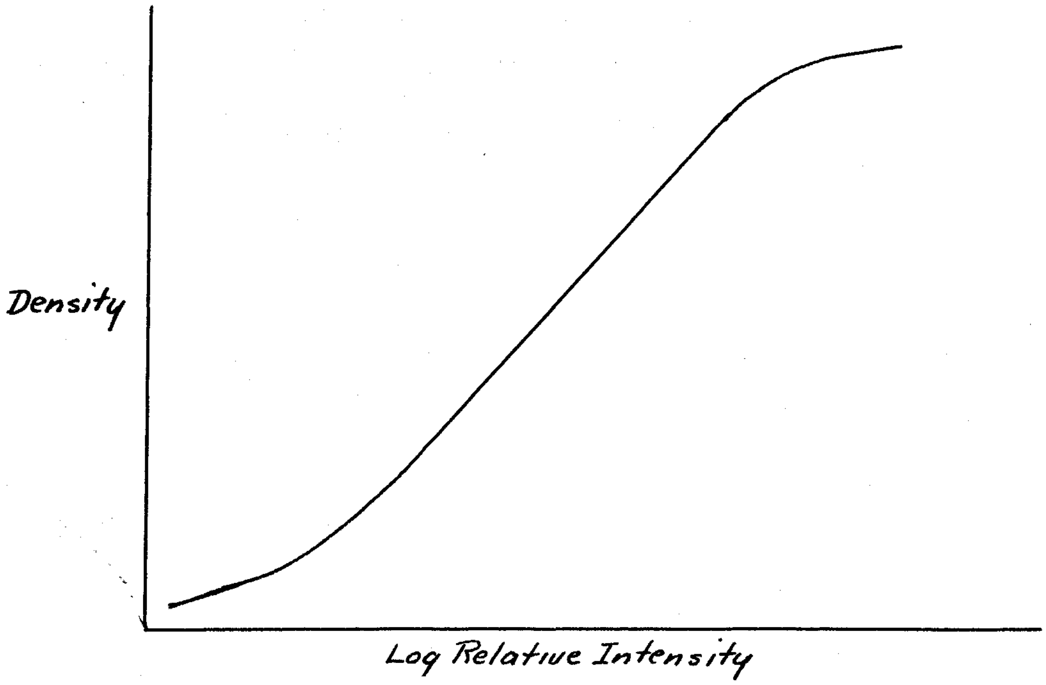

Figure 1. Emulsion Characteristic Curve

The basis for the above method of plotting plate response lies in the fact that the curve obtained possesses a linear portion whose slope is called the gamma of the plate emulsion. For many years photometric measurements were restricted to this straight line portion of the curve and relative intensities were calculated by assuming that $\log T = \gamma \log I$, where γ was the slope and <u>T</u> the ratio of the galvanometer deflection of the microphotometer for the clear plate and the line image.

Deflection ratios were thus used in place of intensity ratios. Modern techniques, which possess wider scope and greater accuracy, involve the actual calibration of the photographic emulsion in terms of relative intensities, i.e., the determination of the actual H and D curve. This emulsion calibration is made by imposing on the plate a graduated set of intensities of the wavelength of light being measured and determining the data for calculating the density by means of a microphotometer. The graduated set of intensities may be produced in a number of different ways (91). The principal methods employed at the present time are: (a) a rotating stepped sector (94, 95), (b) the use of groups of iron lines whose relative intensities have been previously determined (96), and (c) the two line method of Churchill (97). Method (a) will be discussed in detail in the experimental section.

Since the shape and slope of the emulsion calibration curve vary with wavelength and type and emulsion, it is necessary to determine the characteristic curves for the different wavelengths and types of emulsion which are used. The time, temperature and character of development also have significant effects on the curve and these variables are precisely controlled by special developing machines (98).

F. Calculations and Calibrations

The relation between the intensity, I, of light emitted within a source, and the concentration, C, of the emitting atom is linear, if there is no self-absorption. That is,

$$I = K\ C \quad (1)$$

where K is a constant. The equation for the internal standard method then is of the form

$$\frac{I_A}{I_B} = K_2\ C \quad (2) \qquad \text{or} \qquad \log \frac{I_A}{I_B} = \log C + \log K_2 \quad (3)$$

where I_A and I_B, respectively, are the relative intensities of the analysis and internal standard lines and C is the concentration of the constituent to be determined. Equations (2) and (3) express the basic assumption of the internal standard method that the concentration is a function of the single variable I_A/I_B. This assumption requires that K_2 be constant only within the concentration range for which the line pair is used. A plot of I_A/I_B as ordinate versus concentration as abscissa on logarithmic paper or coordinate paper will then produce a straight line.

When self-absorption occurs, as it usually does, the relation between concentration and intensity is given by an empirical equation of the form (99)

$$\frac{I_A}{I_B} = K_4C^n \quad (4) \quad \text{or} \quad \log \frac{I_A}{I_B} = n \log C + \log K_4 \quad (5)$$

The value of n is unity when there is no absorption and less than unity when there is absorption. However, as long as K_4 is constant, a straight line of slope n is still obtained when I_A/I_B is plotted as ordinate against concentration as abscissa on logarithmic paper.

The microphotometer data obtained from the spectrograms is in the form of galvanometer deflections or per cent transmission for clear plate, background and spectral lines. This data is converted to intensities through graphical computations by means of the emulsion calibration curve. These intensities are relative and not absolute intensities; but since the ratio of intensities of a line pair is to be determined, the former are entirely satisfactory. The intensity ratios obtained from a series of standard samples of known composition excited under reproducible conditions provides the necessary data for plotting the log I_A/I_B vs log C curve. The concentration of the element in a sample is then obtained by converting the microphotometer data from the sample into intensity ratio and then determining the concentration by graphical interpolation on the log I_A/I_B vs log C curve.

IV. EXPERIMENTAL

A. Apparatus

The emission spectra of the rare earths has been generally characterized as one of extreme complexity. The number of lines observed has of course depended on the type and intensity of exposure. Yost and Russell (100), for example, stated that a change from one configuration to another in gadolinium can give rise to 20,000 lines even if all selection rules are obeyed. This great complexity made it imperative to employ a spectrograph of high dispersion. The spectrograph chosen was the Jaco-Wadsworth (101) 21-foot grating spectrograph manufactured by the Jarrell-Ash Company of Boston, Massachusetts. This spectrograph employs the stigmatic type of mounting first suggested by Wadsworth (102) in which the anastigmatism is obtained through illumination of the grating with parallel light. The light is rendered parallel by a concave mirror which receives the radiation from the slit placed at the focal point of the mirror. The mirror then reflects the collimated beam back to the grating. The plate holder is maintained on the grating normal by locating it at the far end of the bar on which the grating is positioned. All adjustments necessary to change the wavelength region and at the same time maintaining focus according to the Wadsworth-mounting grating equation are made by electrically operated drives furnished with the instrument. The plateholder movements were similarly actuated by means of a motor driven mechanism. A gear reduction and gear shift on the normal plate drive provided a means for making moving plate exposures at speeds of either 5 or 10 mm per minute. This feature was of great value in following the conditions in the discharge during the excitation.

The 6-inch diameter grating was ruled by Dr. Wood at John Hopkins University with 15,000 lines per inch on a highly reflecting aluminum surface evaporated on pyrex. The collimating mirror consisted of an aluminum coating on a pyrex blank.

The dispersion of this instrument was 5.1 Å/mm in the first order, 2.5 Å/mm in the second order, and 1.7 Å/mm in the third order. The spectral range which could be covered was from 1800 Å to 9600 Å in the first order, from 1800 Å to 4800 Å in the second order, and from 1800 Å to 3200 Å in the third order.

Because of the stigmatic feature of this spectrograph, intensity controlling devices and diaphragms for limiting the height of the spectrum could be placed directly in front of the slit.

The external optical system was designed to provide uniform illumination along the slit length and to achieve maximum illumination by insuring that the light entering the slit would fill but not exceed the aperture of the collimating mirror or grating. These conditions were fulfilled by employing a 10.5 cm focal-length cylindrical quartz lens with the axis vertical placed 44 cm from the slit, and a 50 cm focal-length cylindrical quartz lens with axis horizontal placed directly in front of the slit. The latter lens was incorporated into the rotating stepped sector assembly, the sector disk being located between the slit and the lens. The two cylindrical lenses were used rather than a single spherical lens in order that the light fill the grating horizontally without exceeding it vertically. The source itself was 55 cm from the slit.

A projection system was used to aid in the precise alignment of the electrodes on the optical axis. This consisted of an auxiliary spherical glass lens of 10 cm focal length and a screen 18 cm and 41 cm respectively behind the source electrodes. To project the image of the electrodes on the screen, a light projection device (103) was mounted on the optical bench 19 cm in front of the source electrodes.

The rotating sector assembly was of the triple sector-disk type. The outer rim formed a stepped sector having relative exposure ratios of 1.585. The inner part was cut into two 98° apertures with an inner variable aperture disk whose outer rim extended to cover only half of the aperture of the other disk. A movable bracket permitted bringing any of the three portions to the optical center. The sector was rotated by means of a 4400 rpm electric motor.

The water-cooled excitation stand was patterned after the design of Scribner and Corliss (104).

All components of the external optical system including the excitation stand were fastened on the spectrograph optical bench with suitable carriages.

On the basis of the information obtained from the preliminary experiments, a d-c arc of high amperage offered considerable promise as the best compromise of the source characteristics desired for these analyses. The power source for this d-c arc was a General Electric 5 KW compound-wound generator powered by a General Electric 7-horsepower synchronous motor. The terminal voltage of this generator was adjusted by means of a shunt-field rheostat. A special electrical resistance unit was designed and constructed for the adjustment of the current output. This consisted of ten resistance units made of 3/16 x 0.008 inch Copel ribbon (resistance of 0.155 ohms/foot) wound on three slabs of 1/4 inch Transite measuring 16 by 38 1/2 inches. These were mounted in an angle iron cage 39 inches wide, 19 inches deep, 30 inches high in the back and 21 inches high in the front. The sides of the cage were covered with hardware cloth while the slanting top was made of plywood. The rather large size of the unit provided for adequate spacing of the resistors which permitted air circulation to prevent overheating. Copel ribbon was chosen as the resistance medium because of its low temperature coefficient of resistance. Since a temperature change of 10° affected the resistance by less than 0.02% the change of resistance of the resistors during an excitation was negligible. The values of the individual resistance units, the wiring diagram between the units, and the six-terminal Ohmite rotary selector switches that were used are indicated on figure 2. The rotary switches were mounted on the slanting plywood top of the cage. The voltmeter, ammeter, and switch were mounted in a case and located near the optical bench for convenience and for ease of observation of the electrical characteristics of the arc discharge during the excitations.

Table 1 indicates the arc currents that were obtained for the various resistor combinations when used in series with an arc between 1/4 inch graphite and an applied potential of 250 volts.

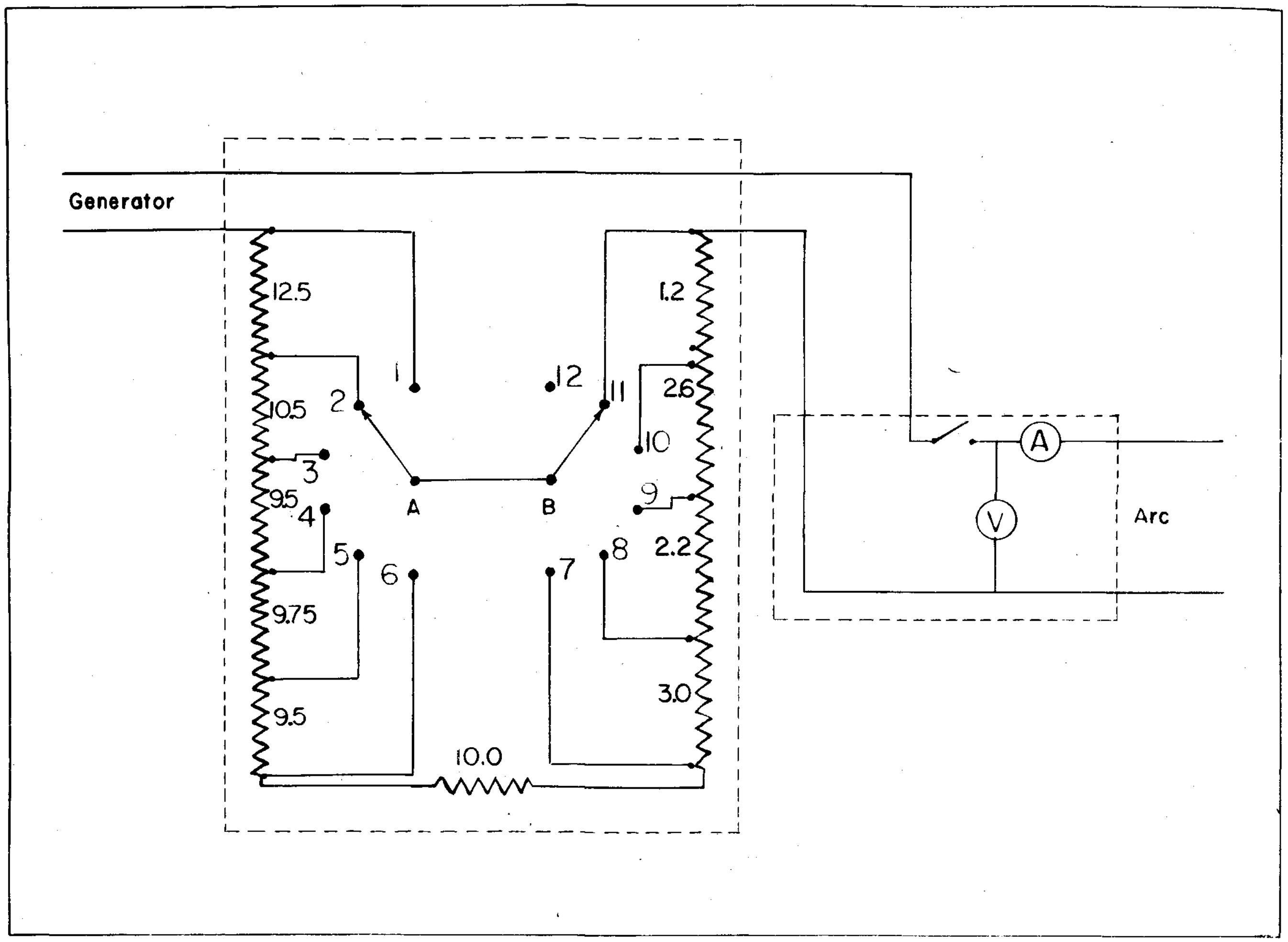

Fig. 2. Wiring diagram for resistance unit and meter box

Table 1

Currents Obtained for Various Resistance Unit Switch Settings

Switch Setting A	Switch Setting B	Current
6	12	2.2 Amperes
6	7	2.7 "
5	7	3.4 "
5	11	4.0 "
4	7	4.4 "
4	11	5.4 "
3	7	6.4 "
3	8	7.0 "
3	9	7.8 "
3	10	8.4 "
3	11	9.0 "
2	7	10.4 "
2	8	12.0 "
2	9	13.6 "
2	10	15.5 "
2	11	17.2 "

For the processing of the spectrum plates an ARL-Dietert developing machine (105) was used. In this machine constant developer temperature (21°C) was maintained by a thermostatically-controlled magnetic cold-water supply valve. A rocking mechanism on the tank containing the developing, hardening, and fixing solution trays provided for uniform chemical action over the entire plate surface.

An ARL-Dietert Comparator-Densitometer (106) was used to measure the density of the spectral lines. In this instrument a slit mechanism scanned the emulsion side of the photographic plate. The light passing through the slit was reflected to a vacuum phototube, the output of which was amplified sufficiently to actuate a galvanometer. The electrical circuit of this instrument was such that galvanometer scale readings could be adjusted to read 0 for infinite blackening and 100 for clear plate and hence gave per cent transmission values directly.

The large fluctuations in the college electrical lines necessitated the use of a voltage regulator to assure constancy of illumination of the densitometer lamp. The frequency variations in the lines precluded the application of the ordinary resonance-transformer regulation, and therefore an electronic regulator (107) whose output was independent of frequency fluctuations was used. The 100-fold electrical regulation factor of this regulator reduced 10-volt line transients to a negligible effect on the densitometer readings.

An ARL-Dietert calculating board was used to facilitate the calculations of relative intensities from the transmission readings on the densitometer.

B. Method of Emulsion Calibration

Before calculations of line intensities could be made it was necessary to calibrate the response of the photographic emulsions to exposure intensities. Two types of emulsion were used in this investigation; Eastman Spectrum Analysis No. 1 and Eastman Type III-0.

The most widely used system of emulsion calibration has been the step-sector method. In this method intensity modulation has been produced by means of a rapidly rotating sector containing stepped apertures of known ratio placed in front of a uniformly illuminated slit. Since this method produced intermittent exposures and did not vary the intensity but the time of exposure it has been subject to the limitations of the reciprocity law, i.e., the reciprocity effect and the intermittency effect (92). However, it has been shown by Webb (108) that for each intensity, emulsion, and wavelength, there existed a critical frequency of flash above which it was quite safe to use intermittent exposures as equivalent to continuous exposures. This critical frequency was of the order of 10 flashes per second. Sawyer and Vincent (109) have shown that for Eastman Spectrum Analysis No. 1 plates sector-disk calibrations at 3000 flashes per minute produced curves which were found, within the accuracy of their measurements, to be self-consistent with curves obtained by the inverse square procedure, the latter being considered the most fundamental method. No data about the properties of the Eastman Type III-0 emulsion could be located in the literature, so it was necessary to apply self-consistency tests to determine the extent of reciprocity law failures for this emulsion.

Preliminary tests on the uniformity of illumination along the 16 mm slit length exposed by the 8-step sector indicated a significant variation in density at extreme ends of the slit or line image. The central portion of the slit was, however, uniformily illuminated. No attempt was made to correct for the nonuniformity near the extreme ends, but rather a modification of the preliminary-curve (110) method which required only 4 mm slit length at the center was used. This method was quite similar to the ordinary stepped-sector method except that only two apertures instead of the customary 6 to 8 steps of known ratio were rotated in front of the slit. This produced two-step spectrograms, in which the stronger step was exposed to a relative intensity *r* times greater than the weaker step, *r* being the ratio between the two apertures. A series of spectrograms of increasing exposure intensity were made to provide data to cover the range of densitometer readings encountered in the experimental work. Since the densitometer measured directly in per cent transmission, the series of exposures covered readings between 1 to 98 per cent transmission.

After processing the plates under controlled conditions, the densitometer data were obtained. A typical series of readings from several iron lines in the region 4300-4450 Å photographed on Eastman Type III-O plates is tabulated in Table 2. The apertures used for these exposures were 120° and 196°.

Table 2

Densitometer Data for Preliminary-Curve Method of Emulsion Calibration

% Transmission 120° Aperture	% Transmission 196° Aperture
16.4	2.0
25.0	4.0
40.0	9.5
45.0	10.0
65.0	23.4
76.1	36.2
89.2	66.0
95.5	83.0

The per cent transmission of the 120° aperture was then plotted against the 196° aperture readings. The preliminary curve obtained is represented in figure 3. The final emulsion calibration curve was then obtained from this preliminary curve by selecting as ordinate a per cent transmission higher than any used in the experimental work and arbitrarily assigning to it a relative intensity of one. The per cent transmission of a relative intensity of 196/120 was then determined from the preliminary curve. The latter reading was then applied as ordinate and the per cent transmission of a relative intensity of $(196/120)^2$ read from the curve. This process was continued until a per cent transmission lower than any used in the experimental work was reached. A plot of this data on log-log paper, with per cent transmission as ordinate and relative

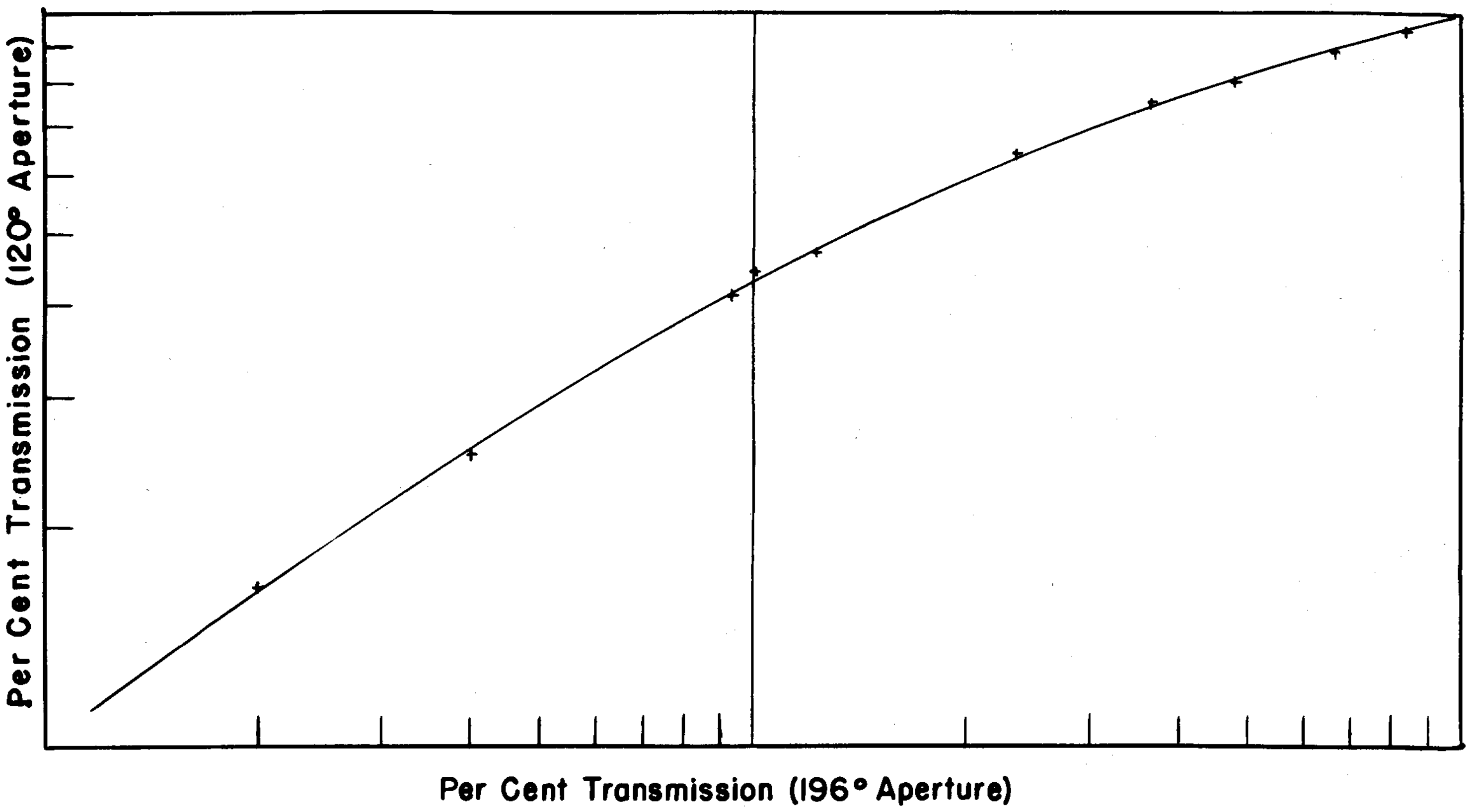

Fig. 3. Preliminary Curve for Emulsion Calibration

intensity as abscissa, produced the desired emulsion calibration curve (Figure 4A) for that wavelength region. Although this emulsion calibration curve was not the customary density versus log relative intensity plot, it was entirely equivalent to the usual calibration curve. This method of plotting was chosen because it was unnecessary to convert densitometer readings into densities prior to any intensity evaluations but the densitometer readings could be used directly.

The iron arc used as the calibration source was a Pfund-type arc described by Slavin (111).

To determine the seriousness of the possible reciprocity and intermittency effects for the Eastman III-0 plates calibration curves were determined by: (a) the two-step sector with iron line radiation as described above, (b) two-step sector preliminary-curve method with continuous radiation from an incandescent tungsten filament lamp, and (c) time variance of exposure. The source for (c) was a tungsten filament lamp operated from a constant voltage generator. The three curves (see Figure 4) obtained were found to be equivalent within experimental error, and therefore the reciprocity and intermittency effects were negligible. Accordingly, emulsion calibrations for both the Spectrum Analysis No. 1 and III-0 plates were henceforth made by the iron arc, two-step, preliminary-curve method. These emulsion calibrations were repeated at

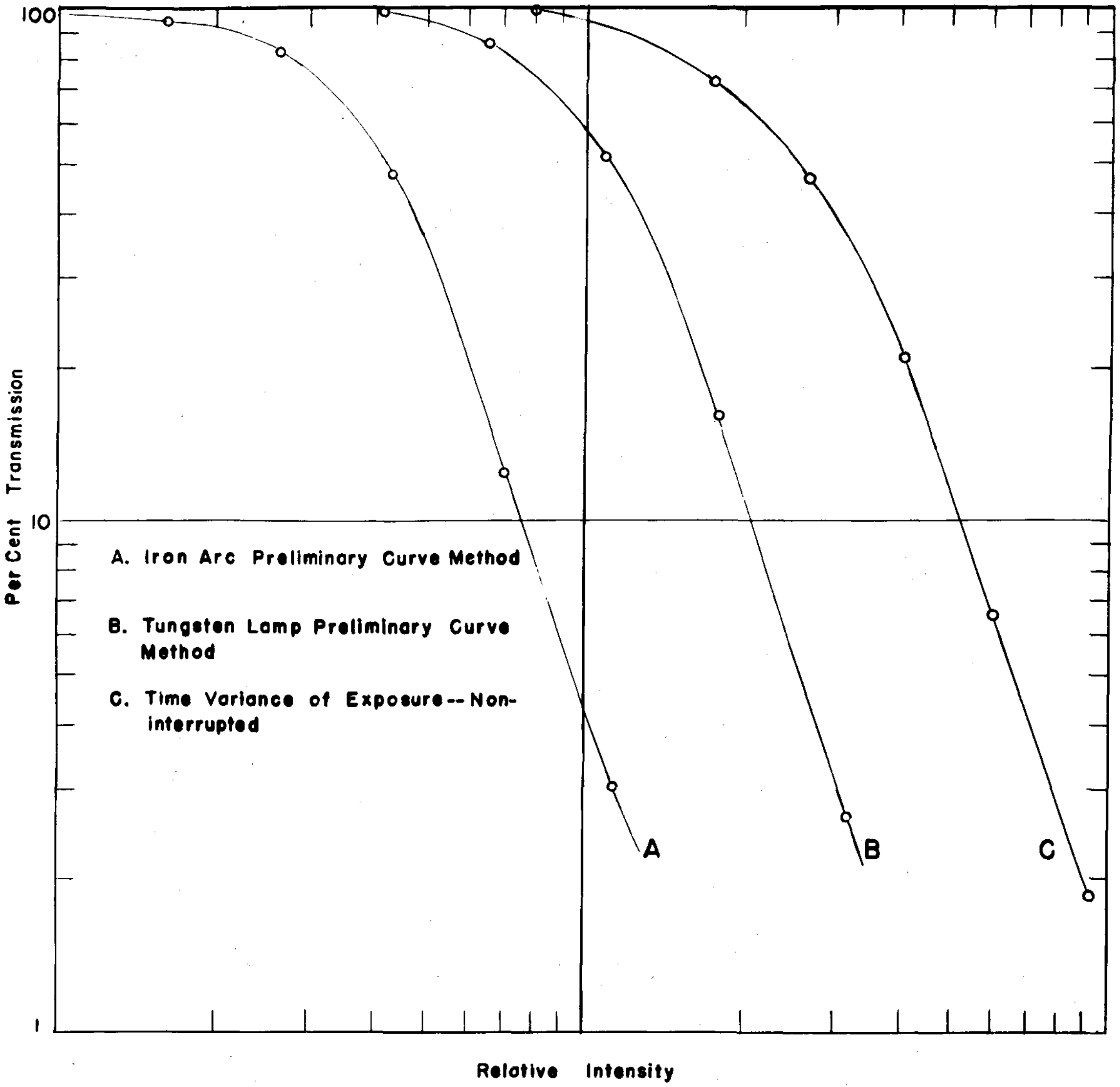

Fig. 4. Emulsion Calibration Curves for Eastman Type 3-O Plates

regular intervals, especially when the plates were manufactured from different emulsion lot numbers.

The developer used throughout this investigation was Eastman D-19. The temperature and time of development were uniformly maintained at 21°C and 4 minutes respectively. The plates were fixed in Eastman F-5, washed for 10 minutes in a plate washer patterned after the design of Vincent and Sawyer (112), and dried in a stream of warm air.

C. Preliminary Experiments

In order to develop methods of analysis of general usefulness, it was necessary to give primary consideration to the chemical and physical forms in which the rare earth mixtures were to be analysed. Whatever the chemical or physical form encountered, it was possible to transform the samples into solutions, various salts, or ignited oxides. Which of these forms would be most suitable was determined largely by consideration of ease of preparation of samples and adaptability to quantitative excitation.

In general, salts have not been found adaptable to direct quantitative excitation. Their low conductivity has prevented the use of a-c arcs or sparks, while thermal decomposition in the d-c arc has produced undesirable sputtering and ejection of the sample from the electrode cavity.

Methods in which solutions flowed or were sprayed into a spark discharge have been described (113, 114). Several undesirable features such as frequent breakdown of the discharge jets and spray corrosion problems have made this technique rather unsuited to large scale applications.

The evaporation of solutions on graphite electrodes, also called impregnation because of the absorbent properties of graphite, was the technique used by Hopkins and co-workers (53) and by Gatterer and Junkes (54) in their investigation on the spectrographic analysis of rare earths by d-c arc excitation. Such electrodes generally have not been found susceptible to precise quantitative excitation by d-c arc methods because of the wide fluctuations in emission resulting from the unstable condition of the discharge. The failure of Hopkins and co-workers to obtain successful results and the fact that Gatterer and Junkes used multiple excitations (9 excitations per sample) to cancel out the variations further attested to the need of devising a different technique.

The high-voltage, alternating-current arc excitation of graphite electrodes impregnated with solutions has been successfully used for the applications mentioned on page 19. The use of copper electrodes as a support for the evaporation of solutions with subsequent spark excitation was extensively developed on the Manhattan Project (115). Successful analytical methods probably could have been developed using either of these evaporation techniques, but they were passed over in favor of the method to be discussed subsequently.

The fractions obtained from the resin-column fractionation method contained considerable amounts of citric acid eluant and accordingly an oxalate separation was used in the process to separate the rare earths from the eluate. The oxalate precipitate was then ignited to the oxide. The logical choice of sample form therefore was the ignited rare earth oxides, because no sample preparation was necessary. The relative ease with which fractions from any other fractionation procedures could be converted to oxides also favored this preference. In addition, most of the chemical methods of separating the rare earth group have involved the precipitation of the oxalate, carbonate, or hydroxide followed by ignition to oxide. However, the refractory properties of the rare earth oxides restricted the type of excitation to the d-c arc, for it alone produced temperatures high enough to vaporize the oxide into the discharge zone. But it was indicated on page 18 that the large experimental errors associated with the general erraticness and poor reproducibility of the d-c arc have limited the application of this source to quantitative analysis. On the other hand, recent studies in several laboratories (116, 117, 118, 119, 120) have shown that in some cases these defects of the arc discharge could be reduced by the judicious use of spectroscopic buffers, internal standards, and special types of electrodes. The plan of attack therefore was to examine the factors affecting the large intensity fluctuations in the d-c arc excitation of rare earth oxides and to develop means of reducing these variations sufficiently to permit quantitative excitation.

The intensity of a spectral line radiated in a hot gas has been described by an expression of the form (121)

$$I_A \sim N_A P_A e^{-\Delta E_A / KT} \qquad (6)$$

and

$$I_B \sim N_B P_B e^{-\Delta E_B / KT} \qquad (7)$$

where $I_A + I_B$ = the respective intensities of the line of element to be determined (test element) and the line of the internal standard.

$N_A + N_B$ = the respective number of atoms/unit volume of test element and internal standard.

$P_A + P_B$ = the transition probabilities respectively of transitions giving rise to the lines of the test element and internal standard.

$\Delta E_A + \Delta E_B$ = the respective energy differences of transitions giving rise to lines of test element and internal standard.

K = Boltzmann constant

T = Temperature

This expression indicated that any variations that affected the ratio of N_A/N_B would have a corresponding effect on the intensity ratio I_A/I_B. In the internal standard method it is assumed that concentration is a function of the single variable

I_A/I_B; therefore, variations in N_A/N_B tend to reduce the accuracy of the method. Also, any variation affecting T would give rise to variations in I_A and I_B. Since in an uncontrolled d-c arc, N_A, N_B, N_A/N_B, and T suffer large variations, the problem was to reduce these fluctuations to a minimum.

The thermal phenomena in a d-c arc have been mainly responsible for variations of N_A, N_B, N_A/N_B, and I_A/I_B, especially with respect to time. The elements have volatilized from the electrode crater in the order of the boiling points of the respective components of the sample matrix (122). Unless the vapor tension and transport properties of the element to be determined and the internal standard were equal, this fractional distillation phenomena has produced large time variations in N_A/N_B. It seemed plausible to expect that because of the similarity of the physical properties of the rare earths, the use of a rare earth as internal standard would, more so than any other choice, maintain constancy of the ratio N_A/N_B irrespective of instantaneous variations of N_A or N_B due to distillation effects and temperature variations. According to the intensity expressions (6) and (7) a constancy of N_A/N_B, under isothermal conditions, would favor a constant value of the ratio I_A/I_B for any particular concentration of A. Since the ratio I_A/I_B has been correlated with concentration in the internal standard method, it was anticipated that the choice of another rare earth would effectively reduce errors due to the time variations of N_A/N_B. The determination of whether constancy of I_A/I_B was actually maintained during the excitation was necessarily postponed until a method of excitation was devised which reduced temperature variations to a minimum.

Arc excitation has been shown to be predominantly thermal in character, so changes in effective excitation temperature have caused concomitant changes in light emission. This, too, was indicated by equations (6) and (7). In a d-c arc these temperature variations have been caused mainly by wandering of the cathode spot, which, according to oscillographic measurements by Vincent and Sawyer (121), were accompanied by irregular variations as great as 50 per cent in current and voltage drop. These variations have been minimized by the admixture of suitable "spectroscopic buffers" (123). The latter were substances which maintained an arc of constant character and which aided in the transport of the sample into the discharge zone at a uniform rate. The first series of experiments therefore consisted of an investigation of the conditions necessary to produce a stabilized arc using graphite as electrode support for the rare earth oxides.

The three-piece graphite electrode assembly described by Scribner and Corliss (118) was used in all of the following experiments. This consisted of a 1/8 inch upper electrode (cathode) tapered to a point and the lower electrode (anode) combination of two parts: a graphite pedestal fastened in the electrode clamps and the anode cap mounted on the pedestal through a taper drilled in the end of the anode cap. These electrodes were machined from National Carbon Company Special Spectroscopic Graphite by means of a Jarrell-Ash Company electrode drilling machine and a motor-driven cutter constructed in the machine shop. The electrode separation was adjusted to exactly 4 mm with the aid of the projection system previously described and was maintained at this separation during arcing by means of the controls provided on the excitation stand.

It was found that for even shallow-cavity electrodes, a 18 ampere d-c arc did not provide electrode temperatures high enough to vaporize a sufficient amount of the rare earth oxides to maintain a uniform, stabilized arc. An annoying feature of this direct arcing of the oxide was the formation of mobile beads of the oxide which usually were ejected from the electrode cavity during the excitation.

Following the suggestions of Bauer (52) a number of experiments were then performed in which the rare earth oxides were mixed with other metallic oxides in the hope that the latter would support a stable arc during the sample excitation and aid in transporting the rare earth oxides into the discharge zone during the stable arc period. Essentially, these experiments consisted of preparing 1:1 mixtures of rare earth oxides and other metallic oxides and arcing these mixtures in the following two types of electrodes: Type A, 4 mm deep cavity with wall thickness of 1 mm; Type B, 2 mm deep cavity with 1/2 mm walls. Twenty and fifteen milligram charges were used for Type A and B respectively.

A necessary requirement of these other metallic oxides were that their volatility at the prevailing arc temperature would be greater than the volatility of the rare earth oxide in order that the increased vapor concentration in the discharge zone would stabilize the arc. Since the literature on boiling points of metallic oxides was very meager, relative boiling points were determined by the spectrographic method described by Richardson (122). A number of different mixtures containing about six to ten readily obtainable oxides and several rare earth oxides were prepared and 20 mg charges in Type B electrodes were arced at 17.5 amperes. Constant rate moving plate spectrograms of these arcs were photographed and the order of volatilization was then determined by noting during what period of the arc the various elements appeared in the arc as evidenced by the appearance and disappearance of the respective lines of the elements. In this manner all oxides of less volatility than the rare earths were eliminated from further study. These included such highly refractory oxides like zirconium and hafnium oxide. Also excluded from further study were the highly volatile oxides such as the oxides of arsenic, mercury, bismuth, cadmium, zinc, gallium, antimony and lead. A number of the other oxides which appeared to possess optimum volatility were then studied in more detail by arcing 1:1 mixtures of the rare earth oxides and the other oxides at 17.5 amperes and photographing moving plate spectrograms at the same time. The oxides studied included those of aluminum, calcium, strontium and magnesium. The majority of these successfully stabilized the arc but the moving plate spectrograms revealed that the major portion of the rare earths were actually volatilized immediately preceeding and during the highly unstable sputtering arc following the stable period. In other words, the more volatile oxides were preferentially volatilized during the stable arcing period. When the supply of the more volatile oxide was exhausted, the arc became unstable during the volatilization of the major portion of the rare earth oxides. Figure 5 indicates qualitatively the volatilization rates for aluminum oxide, calcium oxide and neodymium mixtures as interpreted from the line intensities on the moving plate spectrograms. Such a fractional distillation was anticipated but it was hoped that the carrier distillation (118) effect would be more effective in sweeping the rare earth oxides into the discharge zone during the stable period. It was here that the shallow thin-walled Type B electrodes were introduced in an attempt to overcome the fractional distillation effects but no improvement was obtained. Increasing the concentration of the other oxides up to 80 per cent only

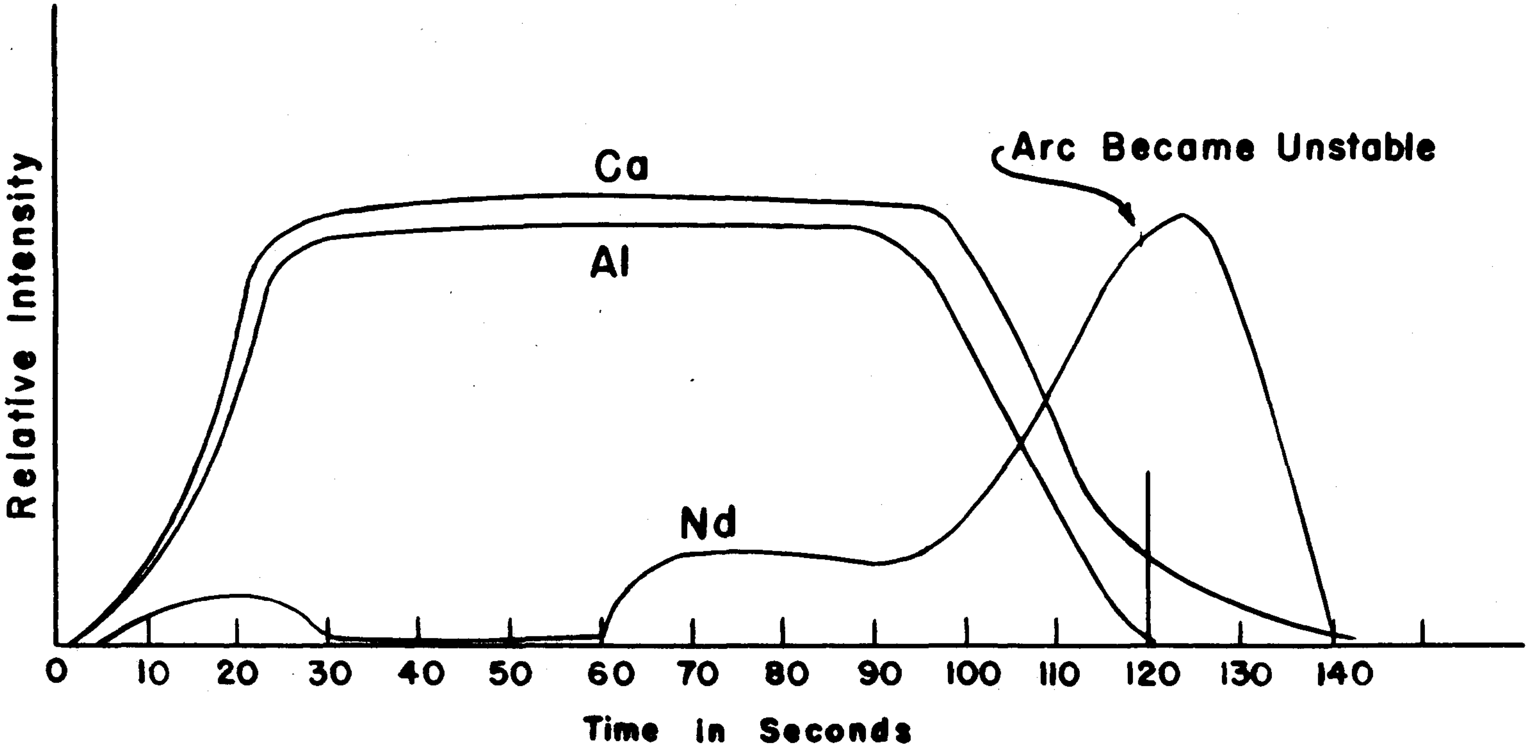

Fig. 5. Volatilization Rates for Al_2O_3, CaO, and Nd_2O_3 Mixtures

prolonged the stable arc period without significantly improving the defects noted above.

Similar experiments were then carried out in which oxides of only slightly greater volatility than the rare earths were used. Chromic oxide and nickel oxide (NiO) were chosen for these experiments. It was hoped that a balance of arc stabilization and equalization of distillation rates could thus be obtained. A qualitative study of the moving-plate spectrograms showed no significant improvement over the fractional distillation defects. Apparently the extremely hot electrodes served as a true distillation column and the carrier distillation effects were negligible.

Failure to obtain any degree of success with the "spectroscopic buffer" approach to arc stabilization led to the use of a mixture of the rare earth oxides and finely powdered graphite (72) in the hope that reduction of the oxide or the intermediate formation of carbide followed by the thermal decomposition of the latter would form the more readily vaporized rare earth metals. The initial experiment consisted of the arcing at 17.5 amperes of 10 mg of an approximate mixture of 1:1 neodymium oxide and 200 mesh powdered graphite in a Type B electrode. This produced an arc of the desired stable character. Short range changes in the arc current were less than 0.3 amperes while the voltage drop fluctuations across the electrodes were of the order of ± 3 volts on a total voltage drop of 32 volts. A moving plate spectrogram made during the above excitation showed uniform emission with time. These results appeared promising enough to warrant further experiments to determine optimum conditions for producing the most stable excitation conditions. The per cent graphite was varied from 30 to 70%, the size of charge from 9 to 21 mg and the current from 13 to 18.4 amperes. This systematic study indicated that at least 16 amperes was necessary to maintain the desired stabilized discharge conditions. The optimum range of per cent graphite was found to be from 40 to 60, while the size of charge seemed to exert no influence on arc stability but only affected the duration of the stable arcing period. The conditions which were then selected for further study were: current, 17.5 amperes; size of charge, 15 mg; per cent graphite, 50.

Before proceeding with any quantitative calibration experiments, it was appropriate first to determine how well the choice of another rare earth as internal standard would fulfill the desired qualification of maintaining a constancy of the analytical ratio during the excitation period as discussed on page 47. To provide the necessary data for these tests the following experiments were performed. Since the first method of analysis to be developed was the determination of small amounts of samarium oxide in purified neodymium oxide, a synthetic standard containing 0.9% samarium oxide in neodymium oxide was used for this experiment. This standard was excited under the optimum conditions as listed above while interrupted type moving-plate spectrograms were photographed. It was not possible to use the constant-rate moving-plate spectrograms for photometric measurements because the vibration of the plate-movement motor generated enough vibrations in the spectrograph to produce ill-defined, fuzzy tracings. These tracings were quite satisfactory for visual observations, but were not suited for photometric measurements. It was possible, however, to rack the plateholder in 3 mm steps at regular intervals by the normal plate drive. This operation required about 3/4 seconds. The spectrograms obtained in this way integrated the intensity ratio for the selected time intervals, which were usually 5 seconds, but were occasionally varied to intervals which would yield line intensities which could be measured with the densitometer. The line pair chosen for measurements was the samarium line at 4433.884 Å and the neodymium line at 4436.68Å. (The procedures used in selecting suitable line pairs will be discussed in detail later). The per cent transmission of the lines were read on the densitometer, the relative intensities determined from the characteristic curve and the intensity ratios then calculated. The data from four such interrupted moving-plate spectrograms were combined and plotted. The curve obtained is reproduced in figure 6. It was surprising to find such a large change in the ratio during the first 15 seconds. This variation was not only shown by the line pair plotted in this curve but also by other pairs, so apparently

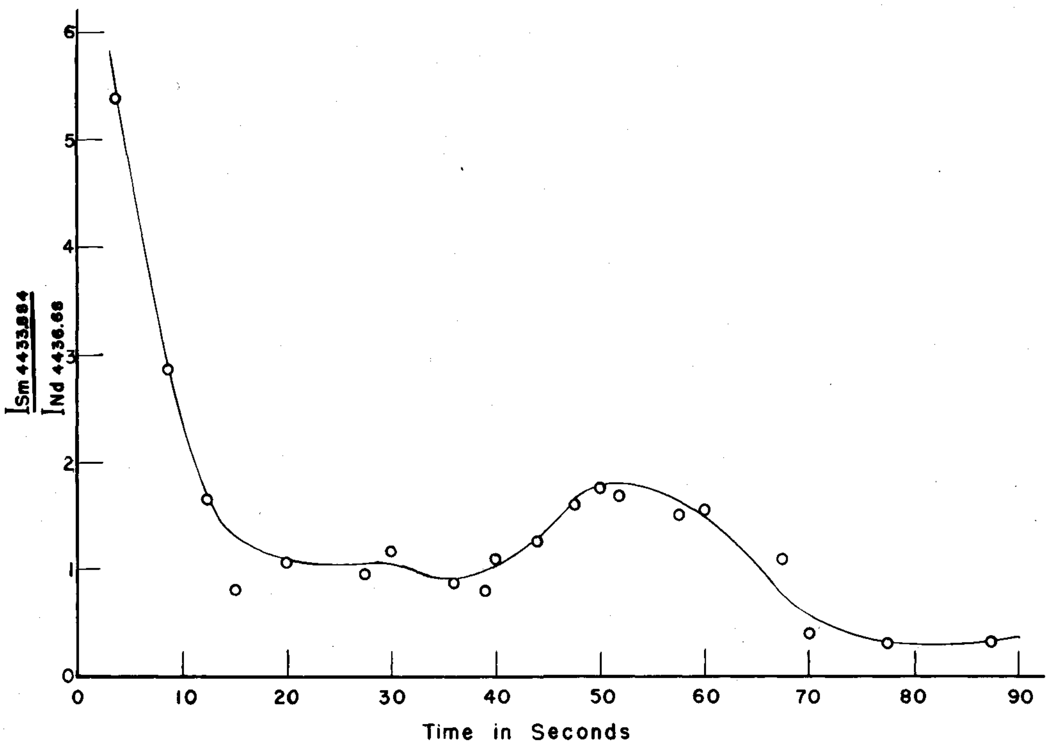

Fig. 6. Variation of Analytical Ratio with Time: Samarium in Neodymium

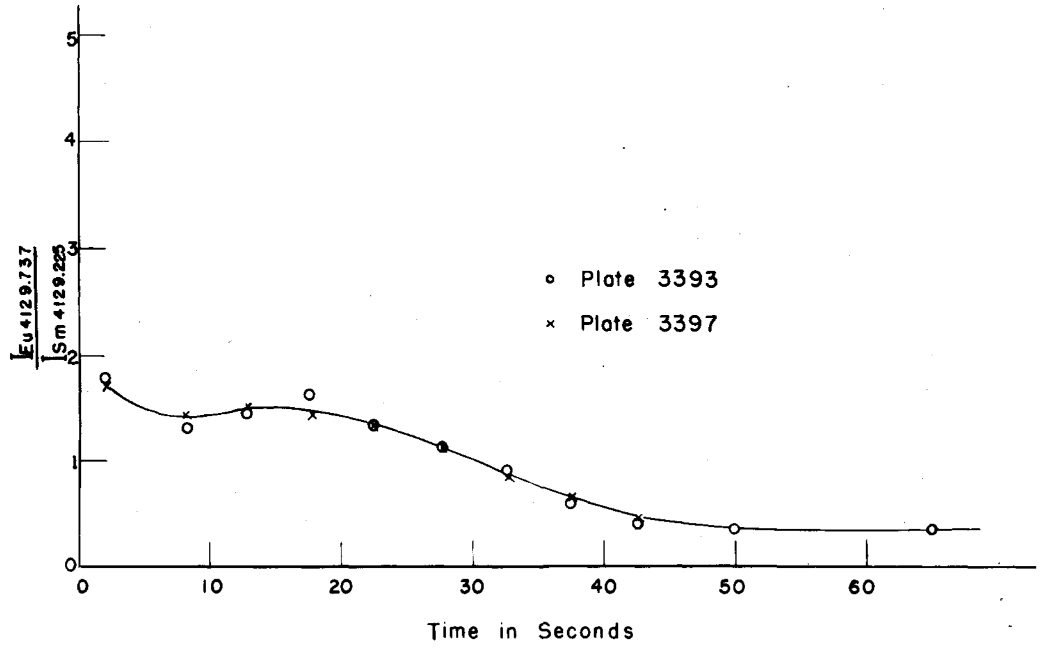

Fig. 7. Variation of Analytical Ratio with Time: Europium in Samarium

the ratio N_{Sm}/N_{Nd} (see equations (6) and (7)) was undergoing a rapid change presumably through different rates of vaporization of the samarium and neodymium during the initial period of the arcing cycle. Such a dissimilarity of behavior of near neighbors in the group was unexpected. If the vaporization had been purely a fractional distillation a continuous decrease, without the observed increase between 40 and 70 seconds, should have resulted. The increase could have originated either by an increase in the vaporization of the samarium or a decrease in the vaporization of the neodymium. A conceivable mechanism offered for these changes in volatily was that the reaction in the electrode charge may have involved an initial reduction of the rare earth oxides to metal and then carbide formation followed by thermal decomposition of the latter to metal and carbon. A difference in the rates of any of these reactions may have occasioned the observed variations.

Similar experiments were also performed on samarium oxide standards containing 0.5% and 0.2% europium oxide. Two line pairs, EuII 4129.737 Å/ SmII 4133.171 Å and EuII 4129.737 Å/ SmII 4129.215 Å were investigated. For both line pairs and both concentrations, curves of the same character were obtained. The curve for the 0.5% sample and the line pair EuII 4129.737 Å/ SmII 4129.215 Å is given in figure 7. The variation of the ratio with time was quite unlike that of the previous experiment and approached the behavior which was desired and originally anticipated.

Although the intensity ratio changes during the excitation were found to be greater than originally preferred, especially for the case of Sm/Nd, the fact that the intensity ratio versus time curves could be readily reproduced from exposure to exposure indicated that the integrated ratio for any concentration should show similar reproducibility. This was shown to be true by making a number of repetitive exposures of the standards used above and calculating the deviation from the mean. The latter was found to be around 3 to 4 per cent and therefore low enough to warrant quantitative calibration experiments.

D. Determination of Samarium in Neodymium

1. Selection of line pair

The selection of the line pairs for the determination of small amount of a rare earth impurity in another rare earth was rendered difficult by several factors. The line interferences resulting from the extremely complex spectra on the one hand restricted the number of lines of the impurity which could be used while the distribution of the spectral energy between the Ist and IInd spectrum reduced the absolute sensitivity of the remaining lines.

The search for the impurity line of greatest sensitivity and not subject to interference from the major constituent was made by the systematic use of Hartmann diaphragm spectrograms and the published wavelength tables. By photographing the spectra of the following: (1) of pure rare earth A, (2) of a synthetic standard containing a known amount of rare earth B in A, (3) of the pure rare earth B and (4) the iron arc, all the intense lines of impurity B subject to interference from the major constituent A could readily be eliminated. The differentiation of whether a weak line coincidence was due to a weak line of A or a residual impurity of B in A was made by consulting the wavelength tables published in the literature (124, 125). The iron arc spectrogram permitted easy wavelength calculations by interpolation.

The most sensitive samarium line which was not eliminated by neodymium line interference was the line at 4433.884 Å due to singly ionized samarium. It would have been desirable to choose as an internal standard a line of singly ionized neodymium but it was necessary to use weak unclassified lines of neodymium in order to select a line of an intensity intermediate to the intensity range covered by the samarium line. Therefore, it was impossible to select with certainty a line of singly ionized neodymium. In order to reduce the effect of variations in emulsion response both as to wavelength and inhomogeneity of the emulsion characteristics over the plate area, the choice of the internal standard was further restricted to a neodymium line whose wavelength was reasonably near the samarium line. The line chosen was the neodymium line calculated to be 4436.64 Å and reported by Bertram (126) as 4436.835 Å, which, after applying the Rowland correction, gave 4436.68 Å.

2. Quantitative calibrations

The neodymium oxide used as base in the preparation of synthetic standards was a portion of the high purity fractions isolated by the resin-column fractionation technique (1, 2). This sample was found to contain less samarium than the Hilger's Spectroscopically Standarized neodymium oxide prepared by Dr. Prandtl. The samarium oxide used was also isolated by resin-column fractionation (1). Spectrographic analysis of this sample indicated the presence of < 0.2% europium and < 0.2% calcium as the only significant impurities. Twenty mg of this oxide was dissolved in 5% hydrochloric acid and diluted to exactly 200 ml. The standards were then prepared by dissolving known weights of the neodymium oxide in 5% hydrochloric acid and then adding to this solution, by means of calibrated pipettes, known volumes of the standard samarium solution. The rare earths were then precipitated by adding an excess of ammonium hydroxide, and the hydroxide filtered off and ignited to oxide. One hundred mg each of standards containing 0.20, 0.50, 1.0, 2.10, and 5.0 per cent samarium were prepared. The ignited oxides were then mixed with an equal weight of

200 mesh high-purity powdered graphite by grinding for several minutes in an agate mortar. A watch glass with a blown off-center funnel hole was used in transferring the mixture into the electrode cavity.

The experimental conditions which were used in the calibration experiments are tabulated below:

Electrodes: Type B, shallow thin walled
Composition of sample: 1:1 rare earth oxide-graphite mixture
Weight of charge: 15 mg
Generator Voltage: 250 volts
Arcing Current: 17.3 ± 0.2 amperes
Voltage drop across electrodes during arcing: 32 ± 3 volts
Photographic Plate: Eastman Type III-0
Wavelength Photographed: 4000-4600 Å (One 10-inch plate)
Order: 2nd
Filter: Corning #774 (to remove 3rd order 2000-3000 Å)
Slit: 0.03 mm
Sector Apertures: 143°, 90.5° and 57°
Exposure: Entire excitation
Duration of Excitation: Until entire sample was vaporized and excited
Developer: Eastman D-19
Temperature of developer: 21°C
Time of development: 4 minutes

The "end point" of the excitation, i.e., when all the sample had vaporized, was readily detectable by the appearance of the unstable, hissing arc and was also indicated by a sudden drop in the arc current and an increase in voltage drop across the electrode.

Duplicate exposures of each standard were made on two different plates.

Although background correction is generally avoided in spectrographic analysis because of the lack of rigorous correction techniques, it was not possible to do this and still attain the concentrational sensitivity desired. The background correction was made by converting the average per cent transmission of the background on each side of the line to relative intensity by means of the emulsion calibration curve and subtracting this relative intensity from the relative intensity of line plus background as determined by the emulsion calibration curve. Since it was previously shown that the same emulsion calibration curve was obtained from continuous and line radiation, the same curve sufficed for the above calculations. This method of background correction has been the closest approach to a rigorous correction.

The pertinent data obtained from the calibration experiments are summarized in Table 3.

Table 3

Calibration Data for the Determination of Samarium in Neodymium

Standard (% Sm_2O_3)	Relative Intensities I_{Sm}	I_{Nd}	I_{Sm}/I_{Nd}	Mean I_{Sm}/I_{Nd}	% Deviation from Mean
0.233	1.40	2.75	0.51	0.49	4.1
	1.53	3.40	0.45		8.2
	0.97	1.79	0.54		6.1
	0.79	1.70	0.47		4.1
0.582	3.02	2.35	1.28	1.17	8.5
	2.58	2.18	1.18		0.0
	1.87	1.65	1.13		0.9
	1.70	1.57	1.08		8.5
1.16	4.80	2.22	2.16	2.17	0.5
	3.14	1.48	2.12		2.3
	3.40	1.57	2.16		0.5
	6.75	3.02	2.23		1.8
2.33	6.10	1.39	4.40	4.45	1.1
	6.60	1.42	4.65		4.5
	6.25	1.38	4.50		2.2
	7.30	1.71	4.26		4.3

Average Per cent Deviation from Mean: 3.6

A plot of this data on log-log paper gave the straight line plotted in figure 10. If it had not been known that the neodymium oxide contained a small amount of residual samarium impurity this curve would have been accepted as correct, for it followed precisely the mathematical equation (5) given on page 27. However, all the concentration values were in error by a constant but unknown amount; therefore, a correction had to be determined. Equation (2) page 27 indicated that, without self-absorption effects, a plot of intensity ratio versus concentration on coordinate paper should give a straight line, and equation (4) indicated that if self-absorption effects were prevalent a deviation from linearity should result. Since self-absorption effects approach zero as the concentration of the element approaches zero, a plot of intensity ratio versus concentration on coordinate paper gives curves which, regardless of self-absorption effects or deviation from linearity, extrapolate to zero intensity at zero concentration (127). Accordingly, the influence of the constant error in the concentration of the synthetic standards described above caused the coordinate plot of the intensity ratio versus apparent concentration to extrapolate not to zero intensity as the apparent concentration approached zero but to a finite intensity. This is indicated in figure 8. The amount of the lateral shift of this extrapolated line away from a parallel line drawn through the origin then represented the amount of residual samarium oxide present in the original neodymium oxide.

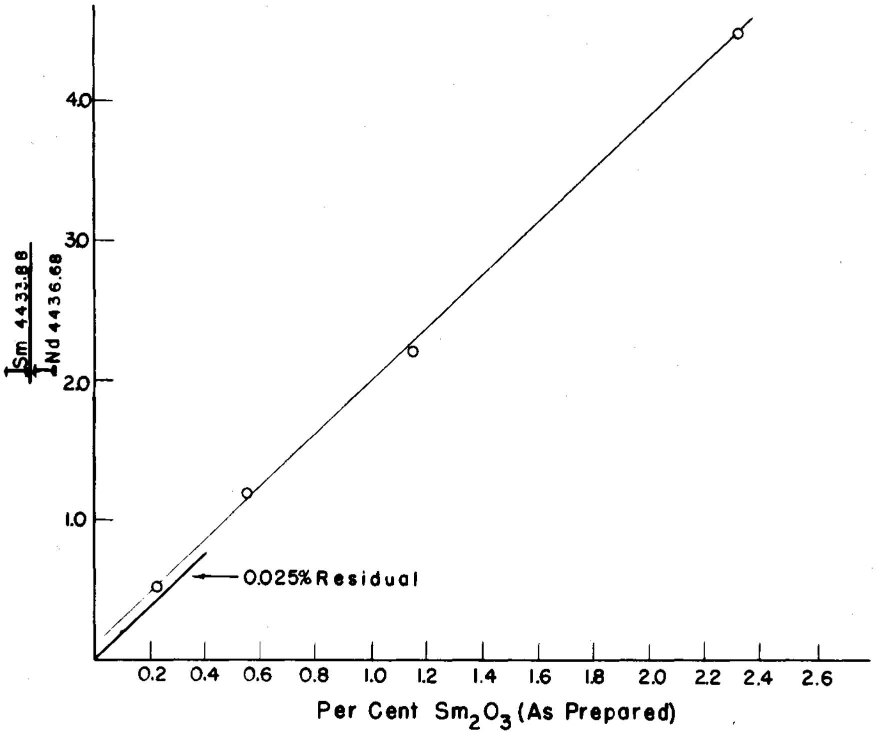

Fig. 8. Residual Correction for Sm_2O_3 in Nd_2O_3 Standards

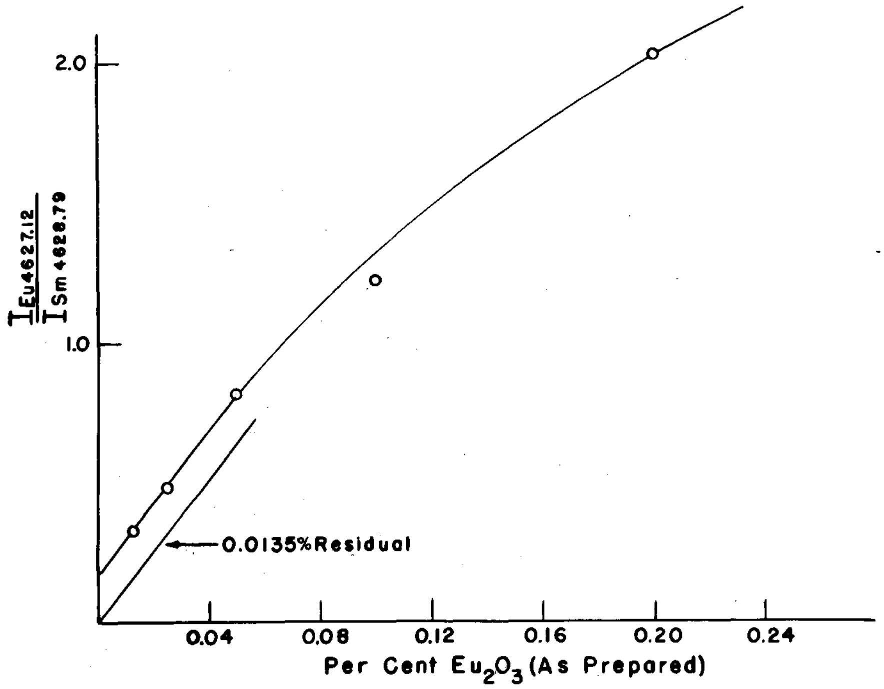

Fig. 9. Residual Correction for Eu_2O_3 in Sm_2O_3 Standards

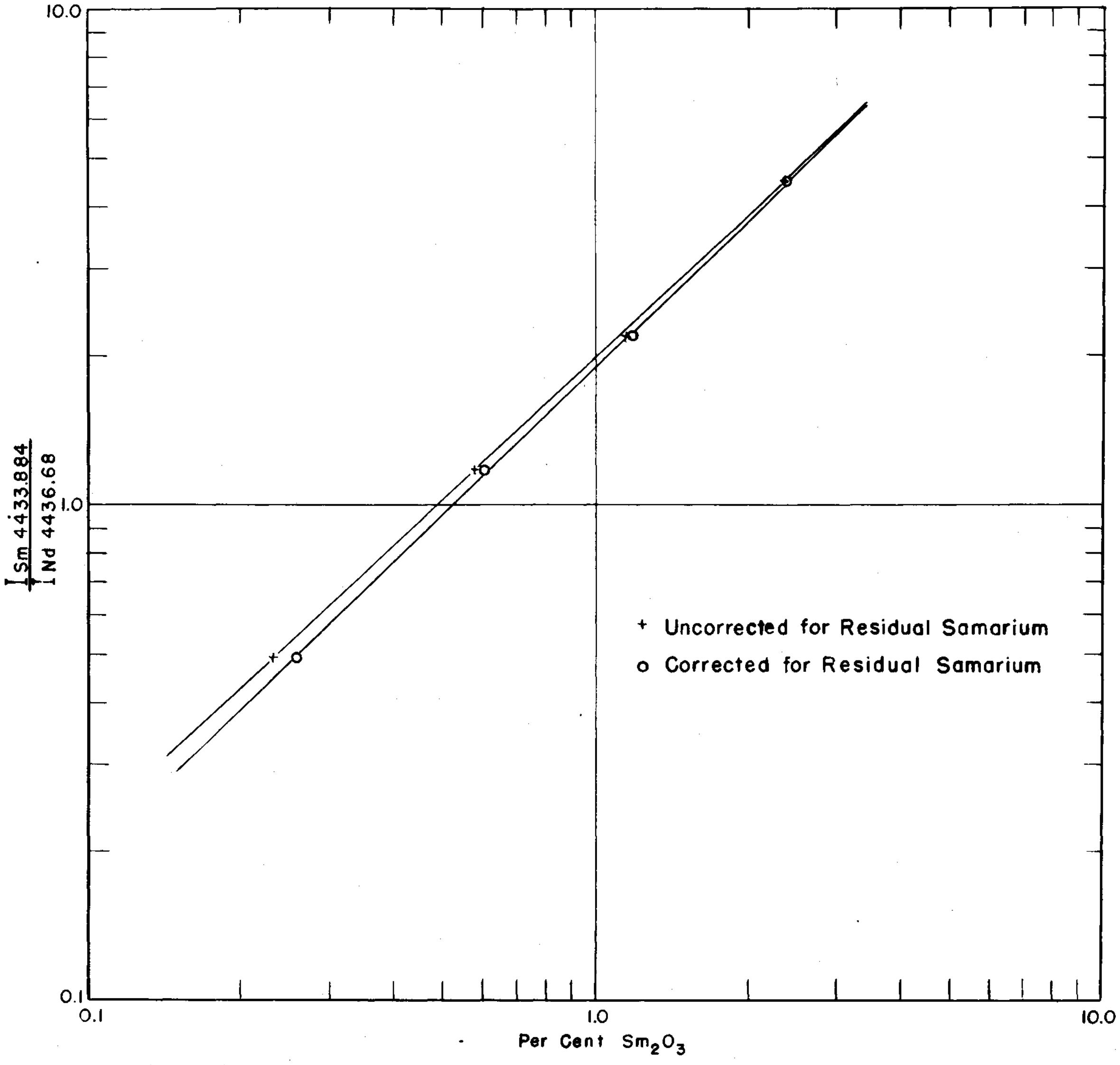

Fig. 10. Calibration Curve for the Determination of Samarium in Neodymium

Introducing this correction to the apparent concentration values gave the corrected calibration curve in figure 10.

These calibration experiments were made with the most careful control of experimental conditions. Since the internal standard technique was designed to reduce to a minimum the effects of accidental or random errors such as light source fluctuations, duration of the stable arc, errors in weighing and transferring of the sample to the electrode, it was of interest to determine how effectively this was accomplished. Several of the variables, namely; arc current, weight of sample charge, and per cent graphite added to the rare earth oxides, were individually changed through ranges considerably greater than ordinarily introduced by random or accidental errors. It was reasonable to expect that the secondary effects of changing the above variables would institute changes greater than those normally encountered in the effective excitation temperature, electrode temperature, duration of stable arc, rates of vaporization, and rates of the chemical reactions in the sample charge. Table 4, 5, and 6, and the curves plotted in figures 11, 12, and 13 summarize the data from triplicate exposures for each of these experiments.

Table 4

Variation of Analytical Intensity Ratio with Arc Current

Arc Current (Amperes)	Average Duration of Stable Arc (seconds)	Intensity Ratio (Average)
13.0±0.2	85	1.42
15.0±0.3	80	1.28
17.2±0.3	78	1.18
18.7±0.3	66	1.20

Table 5

Variation of Analytical Intensity Ratio with Sample Weight

Weight of Electrode charge (mg)	Average Duration of Stable Arc (seconds)	Intensity Ratio (Average)
9	50	1.19
13	70	1.20
15	78	1.18
17	87	1.19
21	105	1.15

Table 6

Variation of Analytical Intensity Ratio
with Per Cent Graphite

Per Cent Graphite	Average Duration of Stable Arc (Seconds)	Intensity Ratio (Average)
30	99	1.16
40	90	1.08
50	78	1.16
60	68	1.26
70	49	1.27

The successful application of the internal standard principle was well exemplified by this data. Even though arc currents below 16 amperes did not possess the desired stabilized characteristics and mixtures containing 30 and 70% graphite produced arcs of considerable unstable character, the data indicated that the effect on the analytical intensity ratio was negligible. The negligible effect of the large variations in weight of sample charge and per cent graphite also showed the noncritical nature of these variables and their associated secondary effects. Precise weighings during sample preparation were therefore shown to be unnecessary.

3. Accuracy and precision

In general, the proof of the accuracy of spectrographic methods has been through comparison of results with those

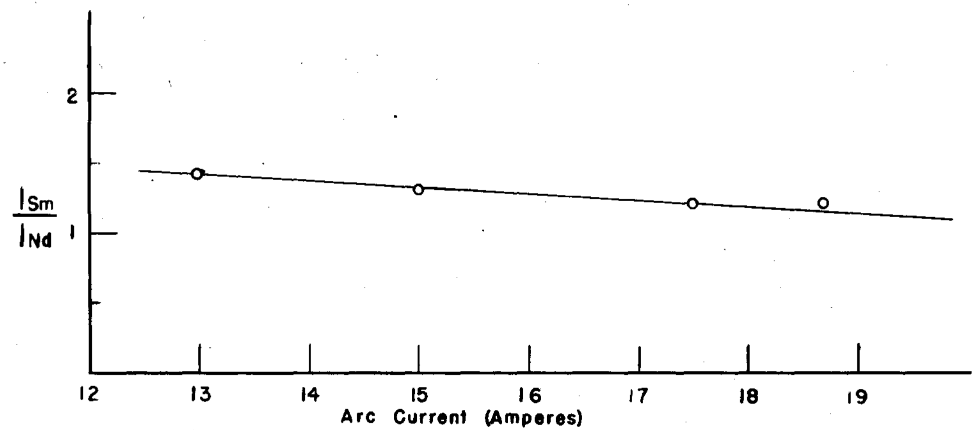

Fig. 11. Variation of Intensity Ratio with Arc Current

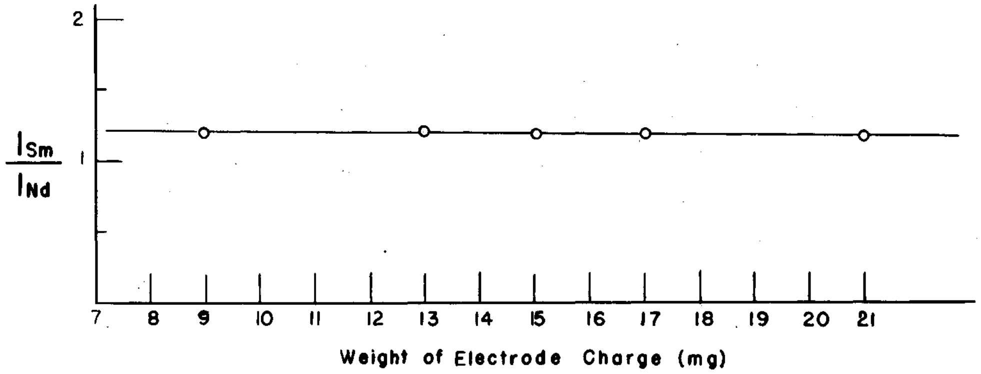

Fig. 12. Variation of Intensity Ratio with Weight of Electrode Charge

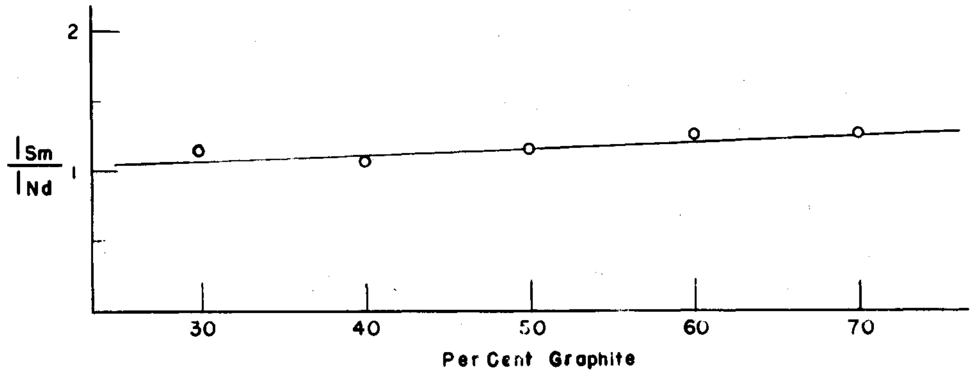

Fig. 13. Variation of Intensity Ratio with Per Cent Graphite

obtained by independent methods of analysis. The inexistence of any independent methods, however, precluded this method of accuracy verification. The next best approach, the so-called recovery experiment method, was therefore used. This consisted of adding known amounts of samarium to portions of previously analysed samples followed by reanalysis of the impregnated portions. Table 7 summarizes the results from a series of ten recovery experiments. Duplicate determinations were made for all analyses.

An indication of the precision of the measurements was shown by the average per cent deviation from the mean of the calibration data tabulated in table 3. Additional data for determining the precision was accumulated by exposing a representative sample in duplicate on nine different plates. These exposures were distributed over a period of about three weeks. The data from these measurements are summarized in table 8. Since the exposure or excitation phase has been one of the chief error producing operations in spectrographic analysis, the significant increase in the precision brought about by making duplicate exposures was not surprising.

The method described above adequately fulfilled the desired qualifications expressed on page 11. There was no reason to believe that this technique could not be adapted to the analysis of other purified rare earths; this conviction was substantiated by the successful adaptation to the analysis of

Table 7

Determination of Accuracy by Recovery Experiments

% Sm_2O_3 (First Analysis)	% Sm_2O_3 Added	Calculated Total % Sm_2O_3	% Sm_2O_3 Found	Error (% Sm_2O_3)	Per Cent Error
0.27	0.20	0.47	0.48	+0.01	2.1
	0.50	0.77	0.80	+0.03	3.9
0.41	0.20	0.61	0.58	-0.03	4.9
	0.50	0.91	0.92	+0.01	1.1
0.18	0.20	0.38	0.40	+0.02	5.3
	0.50	0.68	0.70	+0.02	2.9
0.21	0.20	0.41	0.45	+0.04	9.7
	0.50	0.71	0.76	+0.05	7.0
0.00 (not detected)	0.50	0.50	0.48	-0.02	4.2
0.52	0.50	1.02	1.07	+0.05	4.9

Average Per Cent Error: 4.6

Table 8

Precision of Measurements for the Determination of Samarium in Neodymium

Plate	% Sm_2O_3 Single Exposure	% Sm_2O_3 Duplicate Exposures	% Sm_2O_3 Deviation from Mean (Single Exposure)	% Sm_2O_3 Deviation from Mean (Duplicate Exposures)	% Deviation from Mean (Single Exposure)	% Deviation from Mean (Duplicate Exposures)
3333	1.15	1.06	+ 0.06	- 0.01	5.6	0.9
	0.98		- 0.09		8.4	
3334	1.02	0.98	- 0.05	- 0.09	4.7	8.4
	0.94		- 0.15		12.2	
3337	1.12	1.03	+ 0.05	- 0.04	4.7	3.7
	0.95		- 0.12		11.2	
3345	1.01	1.07	- 0.06	0.00	5.6	0.0
	1.14		+ 0.07		6.5	
3350	1.11	1.11	+ 0.04	+ 0.04	3.7	3.7
	1.12		+ 0.05		4.7	
3351	1.15	1.06	+ 0.06	- 0.01	5.6	0.9
	0.98		- 0.07		6.5	
3355	1.14	1.15	+ 0.07	+ 0.08	6.5	7.5
	1.17		+ 0.10		9.3	
3366	1.11	1.05	+ 0.04	- 0.02	3.7	1.9
	1.00		+ 0.03		2.8	
3367	1.08	1.08	+ 0.01	+ 0.01	0.9	0.9
	1.08		+ 0.01		0.9	

Average per cent deviation from the mean (single exposure): 5.8

Average per cent deviation from the mean (duplicate exposures): 3.3

samarium oxide described in the next section. The experimental error was shown to be less than 5% for duplicate determinations. For ordinary fractionation control the precision of even individual determination was considered adequate. Under normal operating conditions, 4 man-hours provided adequate time for all operations necessary for single analysis of 15 samples or duplicate analyses of 10 samples. The sample requirements were reasonable; only 10 mg were required for a single analysis and approximately 17 mg for duplicate analyses.

E. Determination of Europium in Samarium

1. Selection of line pairs

Preliminary investigations on available europium lines indicated the desirability of using two lines; one for the determination of europium at moderately high concentrations, and another for the determination of europium at maximum sensitivity. The europium line at 4129.737 Å, which originates from singly ionized europium, was admirably suited for the determination of europium oxide in the range 0.1 to 2%. In this concentration range the line exhibited sufficient intensity to permit the reduction of the overall illumination intensity (by means of the variable aperture sector) to the extent that no background correction was necessary. The logical choice of the internal standard was the neighboring samarium 4129.225 Å line since this line not only showed optimum intensity but fortunately also originated from the singly ionized atom. For concentrations below 0.1% europium oxide, this samarium line was too intense for internal standard control. In fact, at the higher intensity of exposure required for the lower europium concentrations, the asymmetric background produced by this samarium line in the vicinity of the europium line rendered the latter unsuitable. The europium line found more suitable for the high sensitivity determinations was the neutral atom line at 4627.122 Å. The samarium line at 4628.794 Å was selected as the internal standard. Background correction was necessary for both individuals of this line pair.

2. Quantitative calibrations

The samarium oxide used as a base for the preparation of the synthetic standards was obtained from the pure fractions isolated by the resin-column fractionation technique (1). This contained only a trace of europium; subsequent residual determination by the graphical method showed only 0.0135% europium oxide still remaining. The standard solution of europium was prepared by dissolving 25 mg of pure europium oxide in dilute 5% hydrochloric acid and diluting the solution to exactly 500 ml. The europium oxide was obtained from Dr. Spedding's collection of rare earths. The standards were prepared in the same manner as described in section IV, D-2, page 60. The series of standards were prepared to contain 0.0125, 0.025, 0.05, 0.10, 0.20, 0.50, 0.99, and 1.96% europium oxide.

The experimental conditions which were used in the calibration experiments for the line pair Eu 4627.122 Å/Sm 4628.794 Å were identical to those tabulated on page 61 except that the wavelength region photographed was changed to 4300-4950 Å. For the line pair EuII 4129.737 Å/SmII 4129.225 Å the conditions again were identical to those tabulated on page 61 except that the sector aperture was changed to 4°. Duplicate exposures[1] of the standards were recorded on two different plates and the intensity determinations made in the usual manner. The pertinent data for the two line pairs is summarized in tables 9 and 10.

It was known that the base samarium oxide contained an unknown residual europium impurity; therefore, a correction for this residual was made by the zero intercept method discussed on page 64. This correction was more precisely determinable by the data for the lower concentration range; namely, for the line pair Eu 4627.122 Å/Sm 4628.794 Å. The graphical plot for this correction is given in figure 9. The curves in figure 14 include both the uncorrected and corrected calibration curves. The corrected curve for the line pair EuII 4129.737 Å/SmII 4129.225 Å is given in figure 15.

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[1] The amount of the 0.5% standard remaining after the preliminary experiments was not sufficient for quadruplicate exposures for each of the line pairs.

Table 9

Calibration Data for the Determination of Europium in Samarium

Line Pair: Eu 4627.122 Å/Sm 4628.794 Å

Standard (% Eu_2O_3)	Relative Intensities I_{Eu}	I_{Sm}	I_{Eu}/I_{Sm}	Mean I_{Eu}/I_{Sm}	% Deviation from Mean
0.0125	0.87	2.92	0.298	0.331	10.0
	1.18	3.20	0.369		11.5
	0.938	2.90	0.310		6.4
	1.11	3.21	0.345		4.2
0.025	1.05	2.08	0.508	0.493	3.0
	1.20	2.50	0.480		2.6
	0.95	1.90	0.500		1.4
	1.08	2.23	0.484		1.8
0.05	1.67	1.92	0.870	0.827	5.2
	1.97	2.42	0.817		1.2
	1.38	1.68	0.822		0.6
	2.58	3.21	0.801		3.1
0.10	2.80	2.33	1.20	1.22	1.6
	2.94	2.35	1.25		2.5
	2.78	2.18	1.27		4.1
	3.34	2.80	1.19		2.5
0.20	4.70	2.34	2.01	2.05	2.0
	5.55	3.06	1.83		10.7
	3.32	1.46	2.28		11.2
	3.02	1.45	2.08		1.5
0.50	4.40	1.63	2.69	2.73	1.5
	5.32	1.94	2.76		1.5

Average Per Cent Deviation from Mean: 4.1

Table 10

Calibration Data for the Determination of Europium in Samarium

Line Pair: EuII 4129.737 Å/SmII 4129.225 Å

Standard ($\%$ Eu_2O_3)	Relative Intensities I_{Eu}	I_{Sm}	I_{Eu}/I_{Sm}	Mean I_{Eu}/I_{Sm}	% Deviation from Mean
0.10	2.25	6.61	0.341	0.359	5.0
	3.03	8.40	0.361		0.6
	3.07	8.20	0.375		4.5
	2.25	6.28	0.360		0.3
0.20	3.05	6.10*	0.500	0.524	4.6
	1.82	3.48	0.524		0.0
	1.93	3.77	0.512		2.3
	2.03	3.64	0.558		6.5
0.50	6.75	7.65	0.883	0.882	0.1
	8.73	9.67*	0.913		1.2
	4.30	5.05	0.850		3.6
0.99	4.83	4.22	1.14	1.21	5.8
	5.05	3.67	1.37		13.2
	9.65	8.15*	1.18		2.5
	4.55	3.90	1.17		3.3
1.96	10.3	5.70	1.81	1.85	2.2
	10.7	5.60	1.91		3.2
	5.95	3.08	1.93		4.3
	8.50	4.80	1.77		4.3

* 6° sector opening

Average per cent deviation from Mean: 3.5

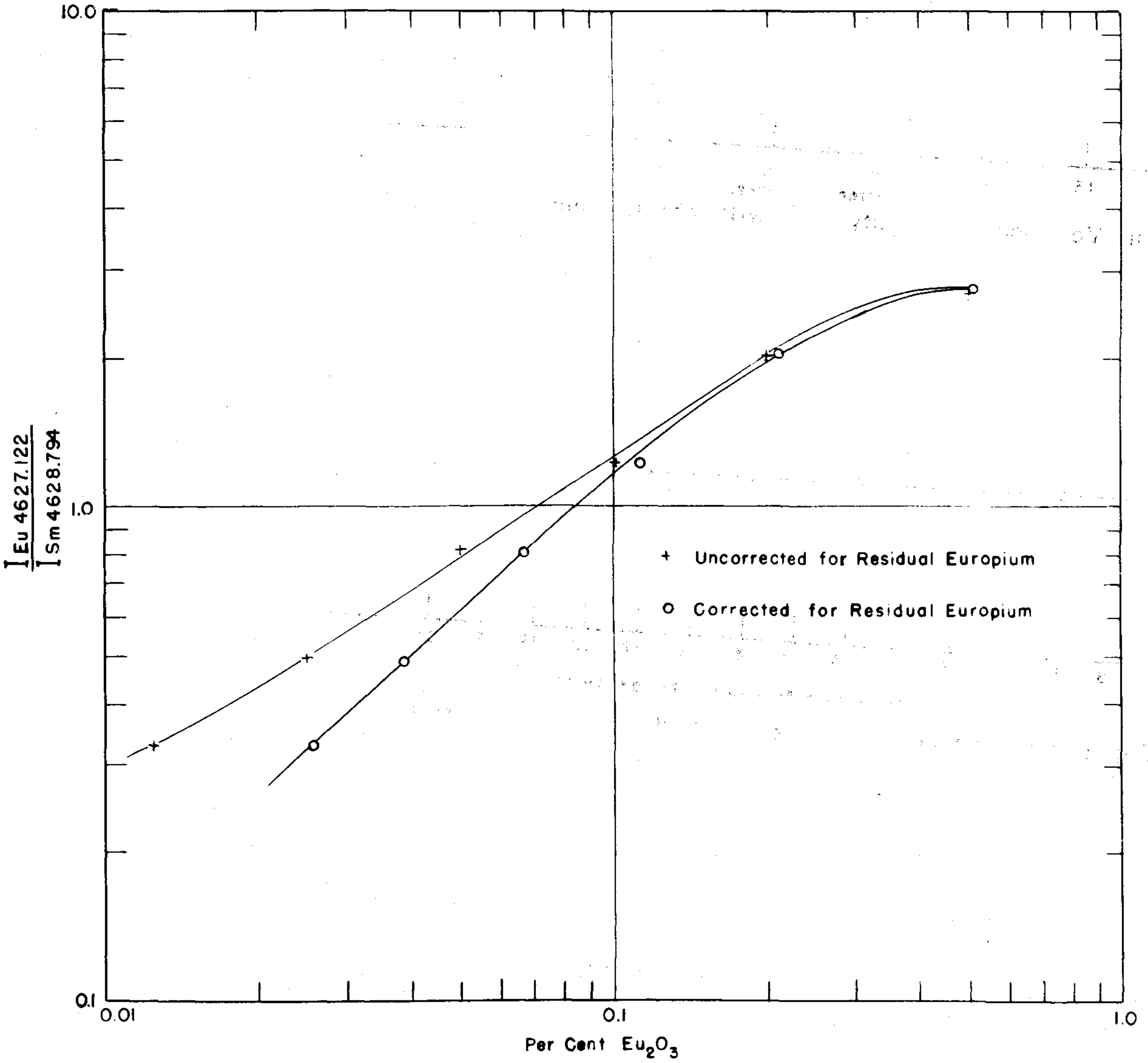

Fig. 14. Calibration Curve for the Determination of Europium in Neodymium

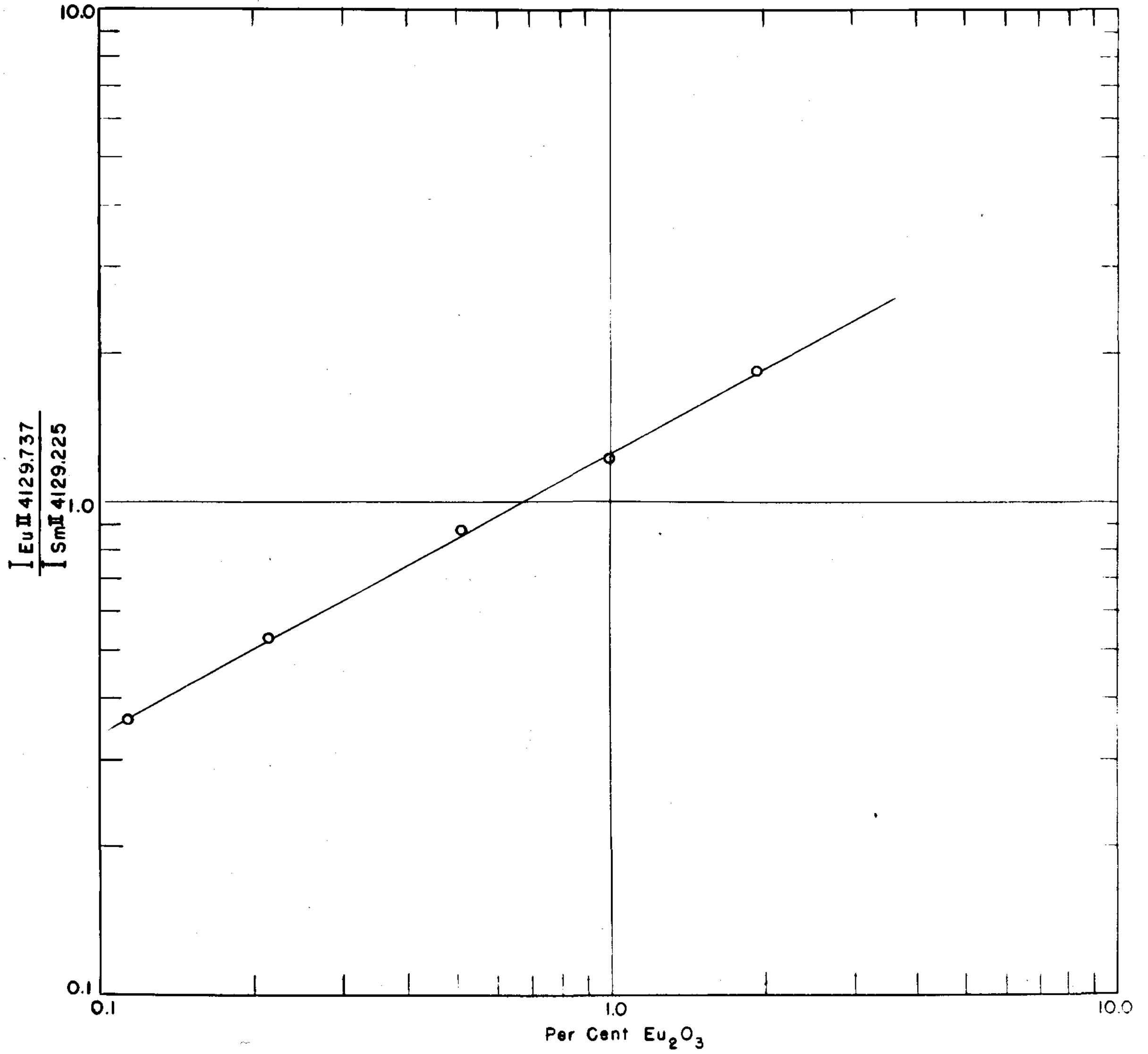

Fig. 15. Calibration Curve for the Determination of Europium in Samarium

No extensive tests were made to determine the effect of the several variables on the analytical ratio as were made in the method for the determination of samarium in neodymium. Since the technique was identical there was no reason to believe that the behavior would be significantly different.

3. Accuracy and precision

The accuracy of both calibration curves was verified by the series of recovery experiments summarized in tables 11 and 12.

No extensive tests on the precision of these methods were made. The average per cent deviation from the mean of the quadruplicate exposures of the standards for the calibration experiments indicated that the precision was comparable to the method described in the previous section.

F. Determination of Large Amounts of Yttrium and Gadolinium in Complex Mixtures

1. Introductory statements

The logical experimental approach to the development of methods for the determination of major amounts of rare earths in complex mixtures was to apply the techniques which were found successful for the determination of minor amounts as discussed in the previous sections. However, certain

Table 11

Determination of Accuracy by Recovery Experiments

Line Pair: Eu 4627.122 Å/Sm 4628.794 Å

% Eu_2O_3 (First Analysis)	% Eu_2O_3 Added	Calculated Total % Eu_2O_3	% Eu_2O_3 Found	Error (% Eu_2O_3)	% Error
0.092	0.025	0.117	0.125	+0.008	6.8
0.070	0.025	0.095	0.097	+0.002	2.1
0.044	0.025	0.069	0.071	+0.002	2.9
0.044	0.050	0.094	0.091	−0.003	3.2
0.012	0.100	0.112	0.107	−0.005	4.5

Average Per cent Error: 3.9

Table 12

Determination of Accuracy by Recovery Experiments

Line Pair: EuII 4129.737 Å/SmII 4129.225 Å

% Eu_2O_3 (First Analysis)	% Eu_2O_3 Added	Calculated Total % Eu_2O_3	% Eu_2O_3 Found	Error (% Eu_2O_3)	% Error
0.34	0.2	0.54	0.57	+0.03	5.6
0.34	0.5	0.84	0.82	-0.02	2.4
0.34	1.0	1.34	1.33	-0.01	0.7

Average Per cent Error: 2.9

complicating factors were immediately evident. In the analysis of purified rare earths for minor impurities it was possible to use a line of the major constituent as internal standard because the concentration of the major constituent remained essentially constant. In complex mixtures, the concentration of all of the rare earths has to be considered as variable and therefore none could be used as internal standard. A solution to this problem was offered by the relative ease with which cerium could be separated from the other rare earths. By first removing the cerium from a mixture and then reintroducing a standard amount, cerium could then be employed as an internal standard. In fact, Hopkins et al. (53) considered this technique but abandoned it because they found that multiple separations were necessary to produce a complete separation of the cerium. Furthermore, the low dispersion of the spectrograph used by these investigators limited the choice of wavelengths to a region which contained too few cerium lines of suitable internal standard intensity. The high dispersion of the spectrograph used in the present investigation eliminated the latter difficulty. In order to circumvent the multiple cerium separations, it was decided to add a large standard amount of cerium so that the cerium remaining after the first separation would be a negligible portion of the total. If cerium were to be added to the sample so that the final composition would be 80% cerium and 20% sample, then cerium concentrations on the order of 1% remaining after the first separation in the original sample would contribute only a small portion to the overall experimental error. Since the cerium separations have been more effective than this, the multiple separations would be eliminated. In the same manner, if the original cerium concentration was 1% or less, no cerium separation would be required.

The addition of a large standard amount of cerium also possessed some secondary features which were highly desirable. In the analysis of mixtures containing varying amounts of one or more elements the interinfluence of the individual components upon each other during the excitations introduced another variable. The effect of major changes in composition on the discharge temperature, heat conductivity, transport and distillation rates has been shown to be significant (128). In view of the similarity in the physical properties of the rare earths this effect was not expected to be significant. Nevertheless, the addition of the relatively large amounts of cerium to the sample would tend to reduce the overall effect of composition changes. At the same time, the reduction of the effective concentration of the element to be determined by the addition of the cerium would aid in reducing the troublesome absorption or self-reversal effects which arise at higher concentrations (129). Another advantage obtained through the addition of the cerium would be the reduction in the sample requirements. The latter would be very desirable in the analyses of mixtures containing the less abundant members of the rare earth series.

2. Preliminary experiments

The ultimate purpose of this phase of the work was directed, as was previously stated, towards the development of emission spectrographic methods for the determination of large amounts of those rare earths which possess no absorption bands in the wavelength regions accessible by ordinary spectrophotometric apparatus and which cannot be readily determined by other methods of analysis. This group consists of lanthanum, yttrium, and lutecium. A method for the determination of yttrium was needed for the ion-exchange fractionation analyses so this member of the group was selected for the initial experiments.

Since the effect of the interinfluence of the components in a mixture was believed to be negligible for the reasons stated on page 85, the following experiments were performed on binary mixtures of yttrium and gadolinium rather than complex mixtures. This not only simplified the preparation of the standards but at the same time provided standards for investigating the determination of gadolinium, although the latter is usually determined spectrophotometrically in the ultraviolet wavelength region. The plan was to study the effect of other rare earth components in complex mixtures after the quantitative calibrations were completed for the simple binary mixtures.

The determination of the constancy of the analytical ratio during the excitation was made by the usual interrupted moving-plate spectrogram method. A sample consisting of approximately 50% each of yttrium oxide and gadolinium oxide was mixed with ceric oxide so that the composition of the mixture was 20% sample oxides and 80% ceric oxide. This mixture was then mixed with an equal weight of 200 mesh powdered graphite. Fifteen mg of this mixture was then excited under the experimental conditions tabulated on page 61 except that the Spectrum Analysis No. 1 plate was racked every 5 seconds. The line pairs chosen for study were the following: for yttrium, YII 4358.726 Å/Ce 4339.317 Å; for gadolinium Gd 4262.095 Å/Ce 4263.427 Å and Gd 4262.095 Å/CeII 4264.370 Å. Two similar moving-plate spectrograms were made on separate plates. The intensity ratios were then determined in the usual manner. Figures 16 and 17 summarize the data which was obtained. The relatively small change in the value of the intensity ratio during the entire excitations, especially for the Y/Ce ratio, approached the idealized condition which is seldom attained in d-c arc methods. This relatively constancy of analytical ratio plus the high reproducibility of the data from the individual plates indicated that cerium excellently

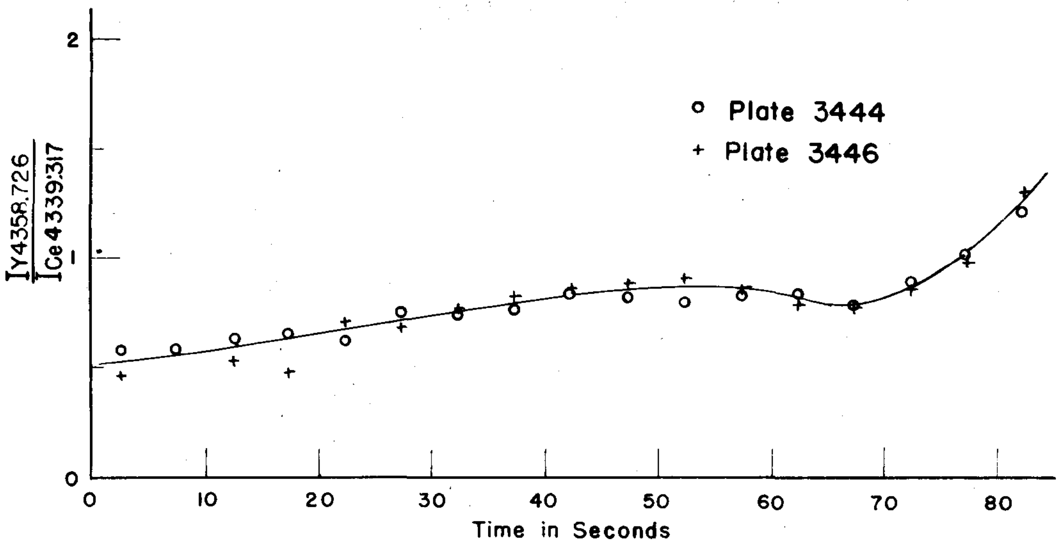

Fig. 16. Variation of Analytical Ratio with Time: Yttrium in Complex Mixtures

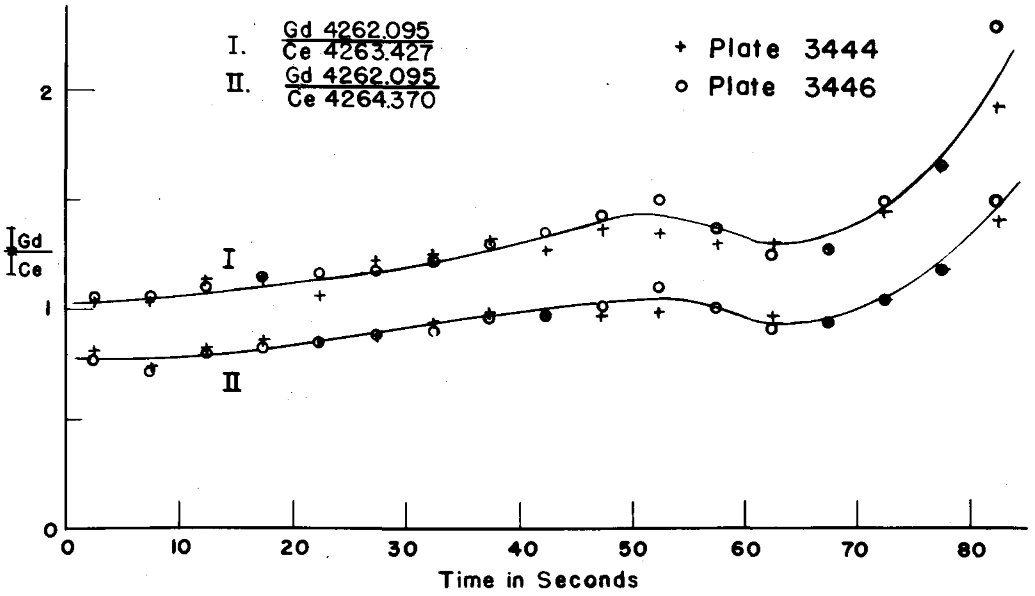

Fig. 17. Variation of Analytical Ratio with Time: Gadolinium in Complex Mixtures

fulfilled the desired qualifications of an internal standard. This was fortunate, for cerium offered the only practical possibility of using another rare earth as an internal standard in these analyses.

3. Selection of line pairs

The search for and selection of suitable line pairs was made in the same manner as described on pages 58 and 59. Special care was taken to select lines least subject to interference from any other rare earths which might be present in significant amounts in actual mixtures containing the yttrium or gadolinium. The line pairs selected were the same that were used for the analytical ratio versus time studies described in the previous section.

4. Quantitative calibrations

The yttrium oxide and gadolinium oxide used in the preparation of the synthetic standards were obtained from Adam Hilger, Ltd, London, England and were of the Spectroscopically Standardized grade. The yttrium oxide (Laboratory No. 6254) came from the collection of Sir William Crookes and the gadolinium oxide (Laboratory No. 13619) was prepared by Dr. J. M. Marsh. A spectrographic examination of these oxides indicated the presence of a trace of yttrium in the gadolinium oxide and a trace of gadolinium in the yttrium oxide. Subsequent tests indicated that the concentration of the respective impurities were negligible. One-hundred mg of each of the above oxides were individually dissolved in dilute hydrochloric acid and diluted to exactly 100 ml. The proper volumes of these solutions were then pipetted into 250 ml beakers to yield solutions consisting of (as oxide) 10%, 15%, 25%, 40%, 60%, 80%, and 100% yttrium while the remainder was gadolinium oxide, i.e. 90%, 85%, 75%, 60%, 40%, 20%, and 0% respectively. The total oxide content of each of these standards was 20 mg. The source of the cerium was ammonium hexanitrato-cerate of primary standard purity sold by the G. Frederick Smith Chemical Company, Columbus, Ohio. A spectrographic analysis of this salt did not reveal the presence of any other rare earths. A standard solution containing the equivalent of 4 grams of ceric oxide (CeO_2) per liter was prepared by dissolving 12.739 grams of the salt in water and diluting to exactly 1000 ml. Twenty ml of the cerium solution were then added to each of the solutions containing the known amounts of yttrium and gadolinium. The solutions were acidified with nitric acid and the cerium reduced by the addition of 5 ml of 30% hydrogen peroxide. An orange brown color developed after the addition of the hydrogen peroxide but this faded quickly to a colorless solution during the subsequent heating. The excess hydrogen peroxide was decomposed by evaporation of the solution to about 10 ml. After diluting the solution to about 100 ml a 5 times stoichiometric excess of ammonium oxalate was added and this was followed by the addition of ammonium hydroxide until the solution was basic. The formation of a brown precipitate at this point was apparently due to incomplete decomposition of the excess hydrogen peroxide. (The presence of hydrogen peroxide in a basic solution containing trivalent cerium oxidizes the latter to the quadrivalent state. The hydroxide of quadrivalent cerium is brown and is not precipitated quantitatively). In the event that the excess hydrogen peroxide was incompletely removed, the solution was acidified with nitric acid and 5 ml of 30% hydrogen peroxide was added to assure reduction of all the cerium oxidized in the basic solution. The solution was then evaporated and treated as outlined above. The rare earth precipitates were filtered off, dried and ignited to the oxides. An equal weight of graphite was then mixed with the oxides by grinding for several minutes in an agate mortar.

The experimental conditions used for the calibration experiments were identical to those tabulated on page 61 except that Spectrum Analysis No. 1 plates were used and the sector apertures were 36°, 22.5°, and 14.2°. The 22.5° aperture spectrograms provided optimum line intensities.

The pertinent data obtained from these calibration experiments are tabulated in tables 13 and 14.

Table 13

Calibration Data for the Determination of Yttrium in Complex Mixtures

Standard (% Yttrium Oxide)	Relative Intensities		
	I_Y	I_{Ce}	I_Y/I_{Ce}
15	1.52	4.75	0.320
	1.55	4.85	0.320
25	1.78	3.68	0.485
	2.12	4.70	0.450
40	2.72	4.20	0.650
	3.14	4.85	0.648
60	4.05	4.80	0.845
	4.00	4.83	0.830
80	4.15	3.86	1.07
	4.85	4.70	1.03
100	4.35	3.62	1.20
	4.00	3.20	1.24

The calibration curves obtained from the data in tables 13 and 14 are illustrated in figures 18 and 19.

5. Accuracy and precision

In order to provide data for determining the accuracy of these calibration curves for the analysis of other than binary mixtures of yttrium and gadolinium oxide, a number of synthetic samples were prepared. These were mixtures prepared by mixing known amounts of yttrium or gadolinium oxide with lanthanum or europium oxide. This provided binary mixtures in which the other components were entirely different from those used in the standards for performing the calibrations. The samples were

Table 14

Calibration Data for the Determination of Gadolinium in Complex Mixtures

Standard (% Gadolinium Oxide)	A Relative Intensities I_{Gd}	A Relative Intensities I_{Ce}	A I_{Gd}/I_{Ce}	B Relative Intensities I_{Gd}	B Relative Intensities I_{Ce}	B I_{Gd}/I_{Ce}
85	4.85	2.68	1.81	4.85	3.60	1.35
85	5.25	2.68	1.95	5.25	3.66	1.43
75	5.65	3.20	1.76	5.65	4.25	1.33
75	4.40	2.45	1.79	4.40	3.42	1.28
60	3.58	2.24	1.60	3.58	3.10	1.15
60	4.15	2.73	1.52	4.15	3.74	1.11
40	3.30	2.70	1.22	3.30	3.70	0.892
40	3.38	2.72	1.24	3.38	3.76	0.900
20	2.30	3.36	0.685	2.30	4.45	0.517
20	2.92	4.15	0.705	2.92	5.25	0.555

Column A: Line pair Gd 4262.095 Å/CeII 4264.370 Å

Column B: Line pair Gd 4262.095 Å/Ce 4263.427 Å

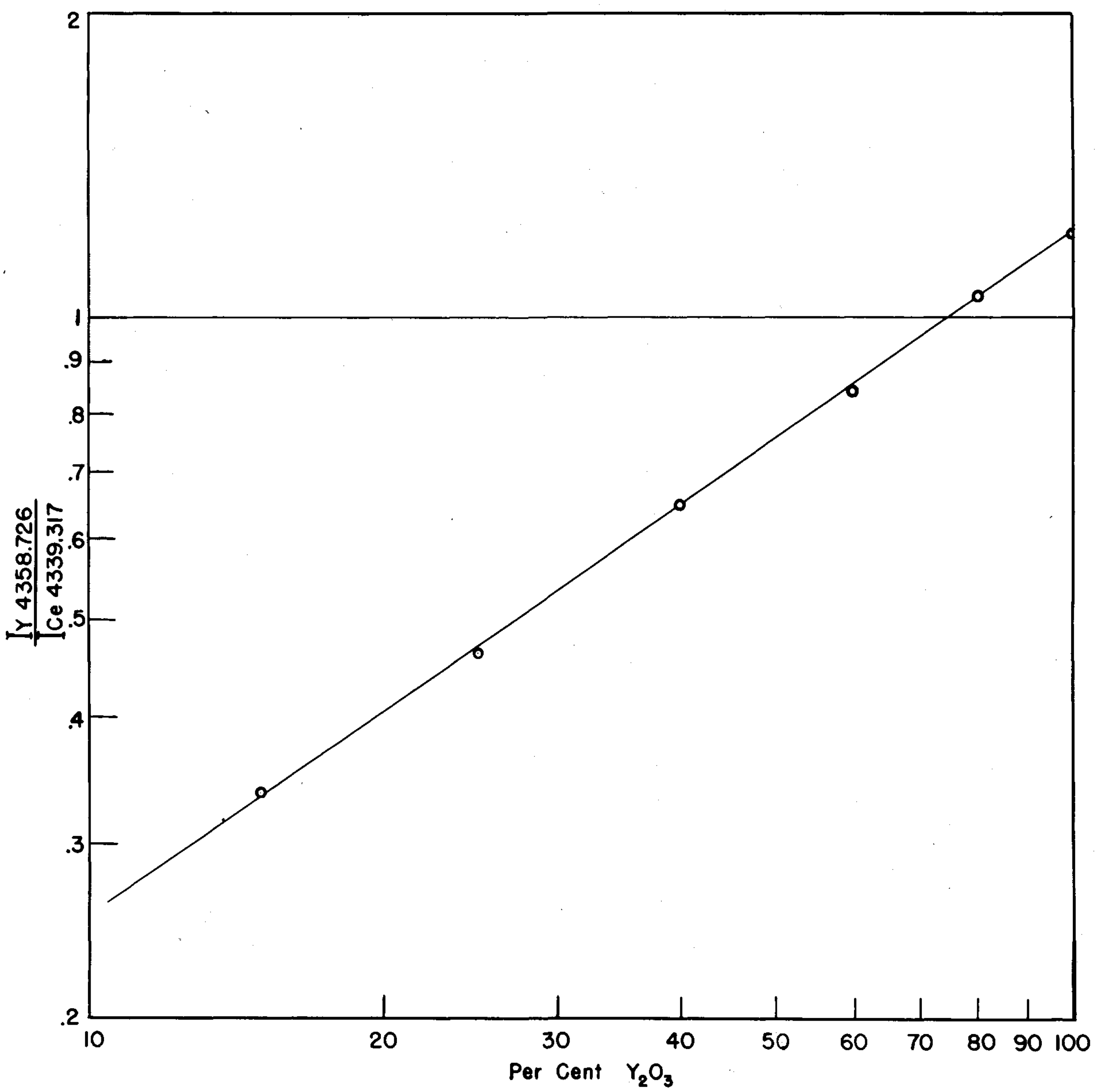

Fig. 18. Calibration Curve for the Determination of Yttrium in Complex Mixtures

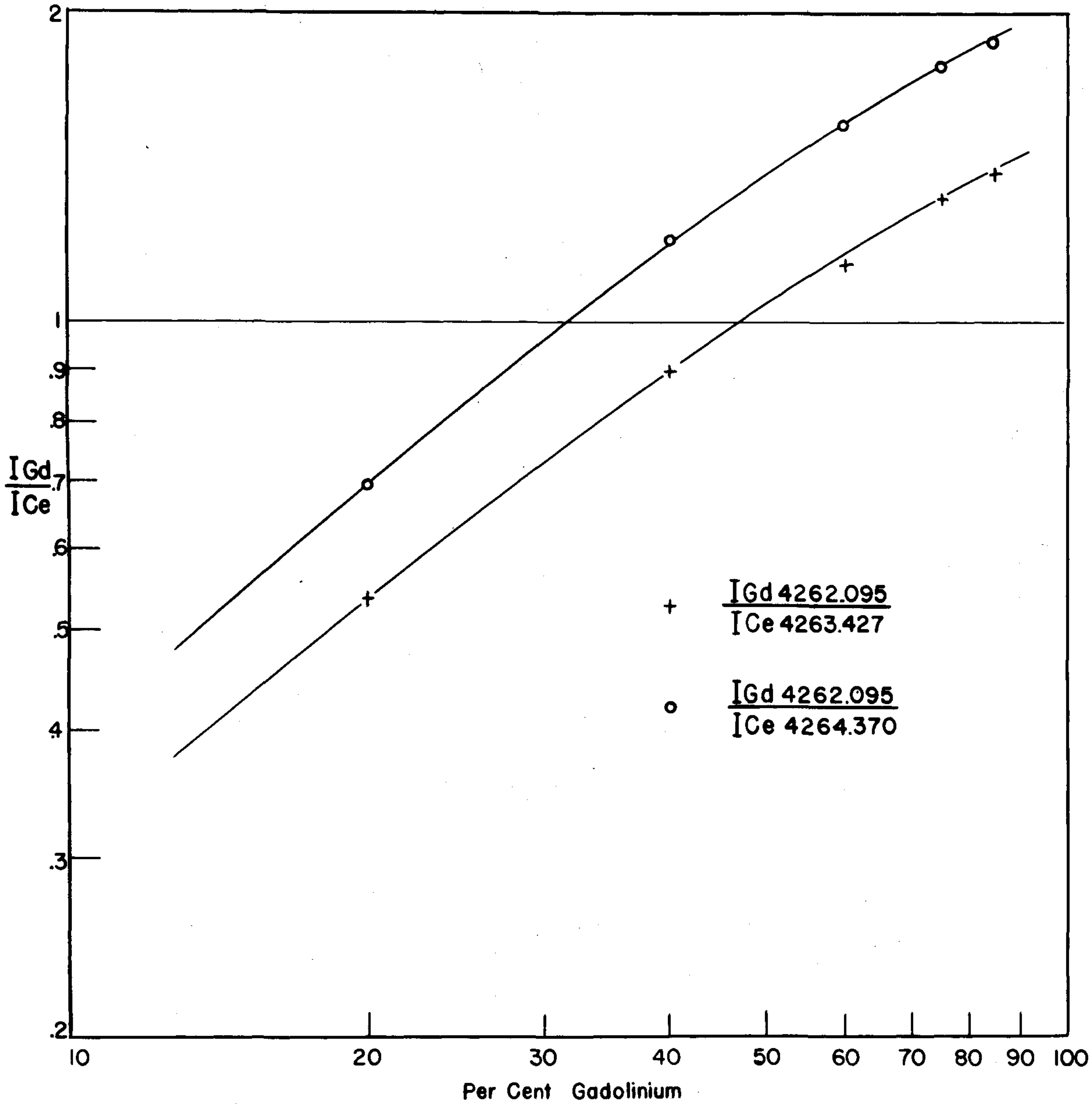

Fig. 19. Calibration Curve for the Determination of Gadolinium in Complex Mixtures

prepared in the same manner as the standards. Duplicate analyses were made on each sample. The results of these experiments are summarized in table 15.

Table 15

Accuracy of Yttrium and Gadolinium Determinations in Complex Mixtures

Composition of Sample	% Yttrium or Gadolinium Oxide Found	Experimental Error (Per Cent)
50% Y_2O_3, 50% La_2O_3	51.0	2.0
50% Y_2O_3, 50% Eu_2O_3	48.5	3.1
25% Y_2O_3, 75% La_2O_3	23.7	5.2
75% Y_2O_3, 25% La_2O_3	76.0	1.3
40% Gd_2O_3, 60% La_2O_3	38.0	5.0

Since the results exhibited an error not greater than the usual experimental error it was concluded that the extraneous influence of the other variable components in the above mixtures was negligible. In view of the great similarity in the properties of the rare earths, it was reasonable to postulate that the influence of any other members of the series would likewise be negligible.

Time did not permit an extensive study of the precision of these methods. The agreement of the duplicate results in the calibration experiments indicated that the precision should be comparable to methods discussed previously.

V. CONCLUSIONS

The successful application of emission spectra to the quantitative analysis of the rare earths has been demonstrated by the development of methods for the determination of minor rare earth impurities in purified rare earths and for the determination of large amounts of rare earths in complex mixtures. The methods which were developed are readily adaptable to the analysis of any purified rare earth or complex mixtures and therefore should find many applications in the analysis of crude ores, fractionation control, and purity determinations.

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