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Determination of Major Constituents in Complex Mixtures

by

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THE QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF THE RARE EARTH ELEMENTS

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ABSTRACT

Spectrographic methods applicable to the determination of major rare earth constituents in complex mixtures are described. The specific examples discussed are the determination of yttrium and gadolinium in the concentration range of 10 to 100 per cent. The procedures involve the high current DC arc excitation of rare earth oxide sample-ceric oxide-graphite mixtures. Selected lines of cerium are used as internal standards. The choice of cerium as internal standard was based on the relative ease with which any cerium, if present in a mixture, could be preferentially separated from the mixture, and then reintroduced in a standard amount. Precision studies show a standard deviation of about ± 2.5 per cent of the amount present. Data are included which indicate that the high precision is attributable to excellent internal standard control of excitation variables.

INTRODUCTION

In a previous paper on this subject,[1] spectrographic methods for the determination of small amounts of rare earth impurities in other rare earths were discussed. These procedures were designed to supplement the useful spectrophotometric methods[2],[3] by providing a means for determining the rare earths below the concentrations detectable by spectrophotometry. Since several of the rare earths, namely, cerium, lanthanum, yttrium, terbium, and lutecium possess no appreciable absorption in the wavelength regions accessible by ordinary spectrophotometers, it has not been possible to determine even large amounts of these members of the group by spectrophotometric methods. Gadolinium possesses an absorption band in the ultraviolet, but background uncertainty and other interferences limit the general usefulness of this band for analytical purposes. Although spectrographic methods are not generally used for the determination of major constituents, the increasing number of publications[4]-[8] on these determinations during the last few years indicate that there are no fundamental reasons which prevent these applications. The very limited scope of chemical and other analytical procedures for the analysis of the rare earths especially favored the extension of the spectrographic method to major constituent determinations. In the present paper a method is described for the determination of gadolinium and yttrium in complex mixtures in the concentration range 8 to 100 per cent. The method is so designed, however, that it should be adaptable to the determination of any major rare earth constituent except cerium.

HISTORICAL

Hopkins and co-workers[9] have investigated the determination of major constituents in rare earth mixtures. Their method was based on the evaporation of rare earth nitrate solutions on graphite electrodes and the excitation of these electrodes with a low voltage DC arc. The variations of their results

were too large for a successful analytical method; the major error was attributed to the poor reproducibility of the DC arc discharge between electrodes prepared in this manner, and to their choice of internal standards.

APPARATUS

The spectrograph, optical system, excitation source, electrode assembly, plates, and photographic processing which were used have been described in detail in the previous paper.

PRELIMINARY EXPERIMENTS

The logical experimental approach to the development of methods for the determination of major rare earth constituents was to apply the same techniques which were found successful for the determination of minor constituents.[1]

In the analysis of purified rare earths for minor impurities, lines of the major constituent were found to be almost ideal internal standards; however, for complex mixtures, the variability in the concentrations of the rare earths precludes the direct use of any of the rare earths present as internal standards. Since tetravalent cerium can be selectively separated from the rest of the rare earths,[10] Hopkins has suggested that any cerium present in a mixture could be removed and then a small, constant amount reintroduced to serve as an internal standard.[9] Hopkins and co-workers abandoned this technique because multiple separations were required to completely remove the cerium originally present. The necessity of completely separating the cerium was circumvented in our investigation by introducing a relatively large amount of cerium rather than the small amount suggested by Hopkins. The ratio of 80 per cent ceric oxide to 20 per cent sample oxide was selected for this study. This ratio permitted another simplification in the procedure, for instead of separating any cerium present, the latter could be determined by standard titrimetric methods[11] on a portion of the sample and then enough cerium introduced into the sample to bring the total cerium concentration up to the standard amount. In general, no preliminary cerium separation is required since the fractionation samples composed of the rare earths for which these methods were designed contain negligible amounts of cerium.

The addition of a large standard amount of cerium also possessed some desirable secondary features. In the analysis of mixtures containing varying amounts of one or more elements the influence 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.[12] 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 amount of cerium to the sample would assist in reducing the overall effect of composition changes on the excitation conditions. At the same time, the reduction of the effective concentration of the elements to be determined by the addition of the cerium aided in diminishing the self-reversal effects which generally arise at higher concentrations. Another advantage obtained by the addition of cerium was the reduction in the sample requirements. This is particularly desirable for the analysis of mixtures containing the less abundant members of the series.

It was of interest to determine how satisfactorily the use of cerium internal standard fulfilled the desired qualification of maintaining a constancy of the intensity ratio during the excitations. A sample consisting of approximately 50% each of yttrium oxide and gadolinium oxide was excited under the experimental conditions tabulated in Table 1, except that the plate was moved every 5 seconds. The intensity ratios on the spectrograms were then determined in the usual manner. Figures 1 and 2 summarize the results obtained. The relatively small change in the ratio during the entire excitation approached the ideal conditions seldom obtained in DC arc work. The curves also indicate the relatively high reproducibility of the ratios from exposure to exposure.
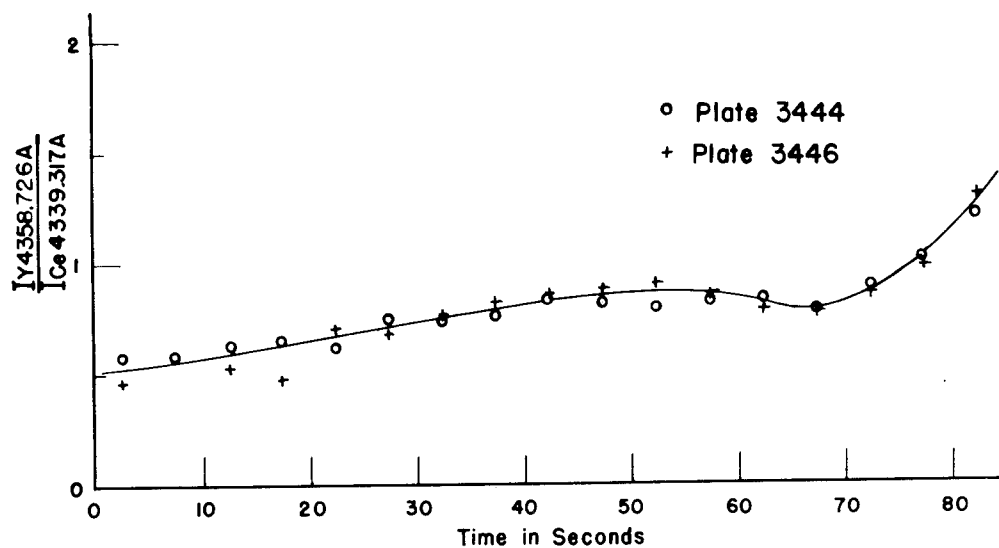
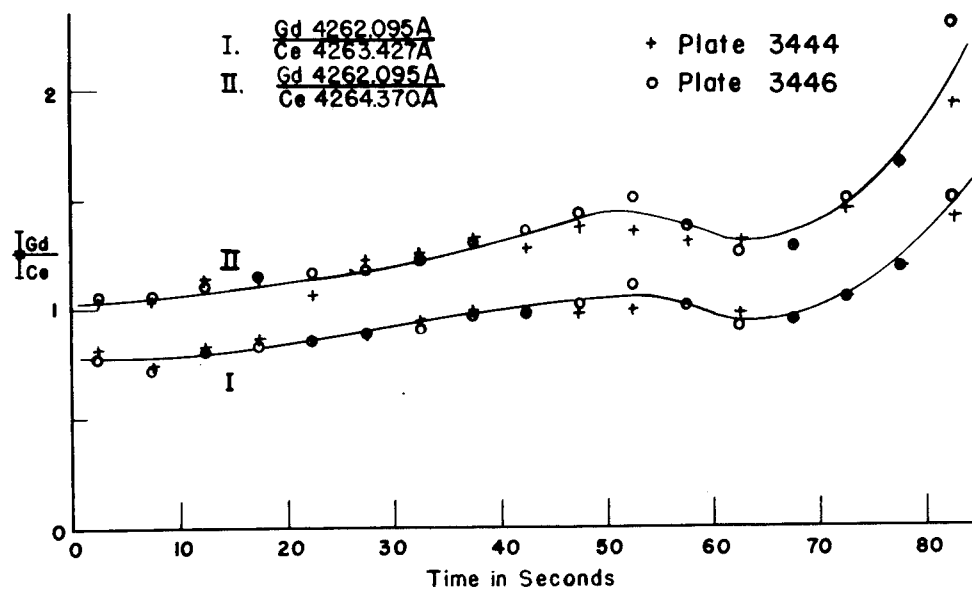Figure 1. Variation of analytical ratio with time: Yttrium in complex mixtures.

Figure 2. Variation of analytical ratio with time: Gadolinium in complex mixtures.

QUANTITATIVE CALIBRATIONS

Preparation of Standards

The initial series of standards was prepared from Hilger's Spectroscopically Standardized, yttrium oxide (Lab. No. 6254) and gadolinium oxide (Lab. No. 13619). After purer fractions became available through the ion-exchange fractionations being carried out in this laboratory,[13] the original calibrations were revised. The calibration curves from each series were consistent with each other after suitable corrections were applied on the purity of the base materials (Figures 3 and 4). The source of the cerium was primary standard purity ammonium hexanitrato-cerate sold by the G. Frederick Smith Chemical Company, Columbus, Ohio. A spectrographic examination of this salt indicated that none of the other rare earths were detected.

The standards were prepared by combining known volumes of the standard solutions of the rare earths followed by precipitation, filtration, and ignition of the precipitate to the oxide. The required amount of cerium was added in the form of a standard solution of ammonium hexanitrato-cerate. Since this solution contained tetravalent cerium, it was necessary to reduce the cerium to the trivalent state in order to coprecipitate the cerium and the other rare earths as the oxalates or the hydroxides. This reduction was carried out by acidifying the cerium-rare earth solution with nitric acid and then adding a stoichiometric excess of 30% hydrogen peroxide. An orange brown color developed upon the addition of the hydrogen peroxide but this faded quickly to a colorless trivalent cerium 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 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 indicative of incomplete decomposition of the excess hydrogen peroxide. (If a cerous salt is precipitated with ammonium hydroxide in the presence of hydrogen peroxide, a reddish-brown precipitate of perceric hydroxide is formed which is not quantitatively precipitated and is not stable.[14] In the event that the excess hydrogen peroxide was incompletely removed, the solution was again acidified with nitric acid and an excess of 30% hydrogen peroxide 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 at 800 to 900°C. An equal weight of graphite was then mixed with the oxides by grinding for several minutes in an agate mortar. In preparing actual samples for analyses, the proper amounts of sample oxide, ceric oxide, and powdered graphite are mixed by grinding for several minutes in an agate mortar.

Selection of Line Pairs

Insofar as possible, line pairs were selected whose components possessed the desired equivalent excitation properties and intensities and proximity of wavelengths. Special care was taken to select lines least subject to interference from any other rare earths which may be present in significant amounts in actual mixtures containing yttrium and gadolinium. The line pairs are listed in Table 1. The excitation potential of the Y 4358.726 A line, which originates in the singly ionized atom is 9.4 electron volts,[15] while the internal standard cerium line, which likewise originates in the single ionized atom, is 10.6 electron volts.[16] King's[17] temperature classification of the Gd 4262.095 A line indicated that it was a blend of two lines in which the violet component originates in one of the higher states in neutral gadolinium while the red component originates in singly ionized gadolinium. The two cerium lines, Ce 4263.427 A and Ce 4264.370 A, both originate in the ionized atoms with excitation potentials of 10.8 and 10.7 electron volts, respectively.[16]

Calibration Experiments

The experimental details used in obtaining the calibration data are summarized in Table 1. The photometric evaluations of the spectrograms were made in the usual manner.[1,18,19] The steps of the sectored spectrograms which possessed the optimum degree of blackening were selected for measurement. No background corrections were required. Figures 3 and 4 illustrate the calibration curves
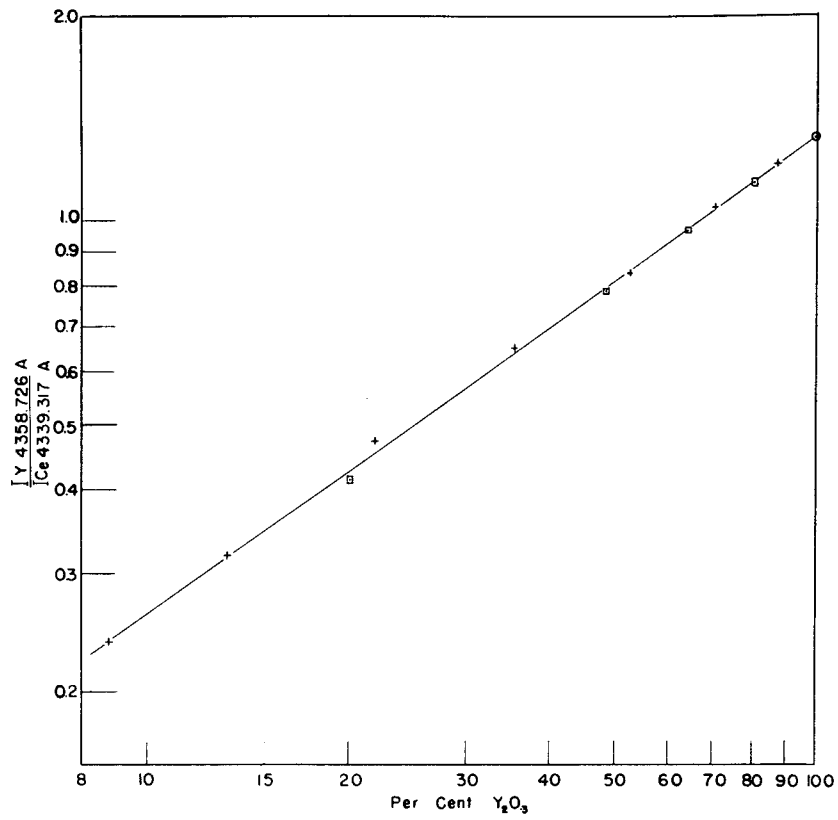
Figure 3. Calibration curve for the determination of yttrium in complex mixtures.
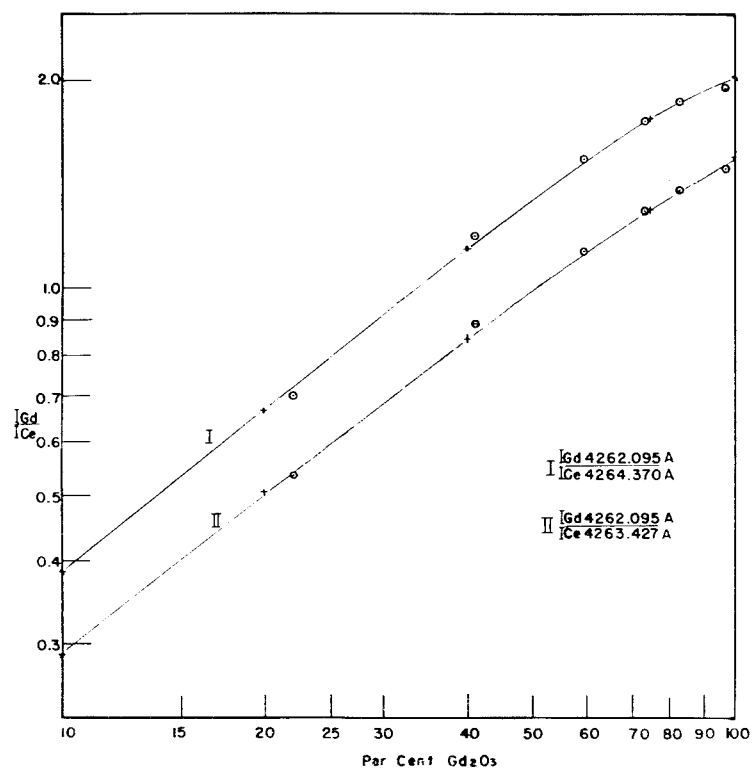
Figure 4. Calibration curves for the determination of gadolinium in complex mixtures.

obtained by plotting log intensity ratio vs log concentration. The two series of points indicate the substantial agreement between the sets of standards previously discussed.

Precision and Accuracy

The data in Table 2 summarize the results obtained from single repeated exposures of several samples. These exposures were made on from five to seven different plates.

The results obtained from the analysis of various synthetic mixtures of gadolinium and yttrium oxide with other rare earth oxide are summarized in Table 3. In addition to substantiating the general accuracy of the calibration curves, these data also indicate that the extraneous influences of large changes in the composition of the mixtures are negligible. The results of some comparative yttrium analyses by the spectrographic and atomic weight methods[20] are summarized in Table 4.

CRITERIA FOR HIGH PRECISION ANALYSES WITH DC ARC EXCITATION

The DC arc between graphite electrodes possesses definite advantages in convenience, general application, and sensitivity as an excitation source for the spectrographic analysis of inorganic materials; but the poor reproducibility usually associated with this discharge greatly limits its quantitative applications. However, the data in Table 2 indicate that DC arc excitation can yield results with a precision comparable to that obtained from other carefully controlled excitation sources. The author is aware of several DC arc methods in which the externally recognizable features of stability, such as constancy of current and voltage drop across the electrodes, are better controlled than in the procedures described in this paper, whereas the standard deviation is larger by a factor of three to four. This indicates that the high precision in this method may be attributed more to excellent internal standard control of excitation variables than to careful control of external excitation conditions. Although internal standard techniques are commonly used in DC arc excitation methods, an examination of most of these methods would no doubt reveal that the essential requisite of similar response of the internal standard line pair to source and other excitation variables is not satisfactorily fulfilled. This is not surprising for several of the variables in DC arc excitation are exceedingly difficult to control through the use of internal standards. Since it appeared that excellent internal standard control was inherent in the method described above, it was of interest to determine quantitatively the extent to which some of the essential criteria of the internal standard principle were fulfilled.

The main source of poor reproducibility of the DC arc lies in its thermal excitation mechanism. This mechanism gives rise to: (a) fractional distillation effects which institute large variations in the analytical intensity ratio during the excitation unless internal standards with identical vaporization characteristics are utilized; and (b) large effective excitation temperature variations produced by wandering of the cathode spot, general arc instability, changes in matrix composition, electrode form, spacing, and heat conductivity, and any other process which affects the amount of heat produced in or transferred from the arc. The fact that the above processes are interrelated makes the excitation process very complicated.

The fractional distillation effects are probably the most difficult to compensate through internal standard control because identity in vaporization response is necessary. The great similarity in the physical properties of the rare earths therefore offers a unique possibility to adequately control this variable. Figures 1 and 2 show the relatively small change in the intensity ratios during the excitations. For systems which differ in their vaporization properties, the individual line intensities exhibit nonparallel behavior and may even change in opposite directions[21] during the course of the excitation and thus give rise to intensity ratios starting from zero and increasing to progressively higher values (or vice versa). It is apparent that as the overall changes in intensity ratios increase during the excitations, the reproducibility of the integrated intensity ratios decrease. Moreover, for nonparallel vaporization behavior, the internal standard cannot effectively correct for short period variations in excitation temperatures.

Table 1. Operating conditions for obtaining calibration data.

Line pairs	Y 4358.726 A / Ce 4339.317 A	Wavelength photographed	4000 — 4625 A
	Gd 4262.095 A / Ce 4263.427 A	Order	2nd
		Filter	Corning No. 774
	Gd 4262.095 A / Ce 4264.370 A	Slit	0.04 mm
		Sector apertures	36°, 22.5°, 14.2° (step sector)
Composition of sample charge	40% CeO_2 10% sample 50% graphite	Duration of excitation	Arced to completion
Wt. of charge	15 mg	Development	4 min at 21°C in Eastman D-19
Type of electrode	Anode: 1/4 in dia. graphite, 3/4 in long with 2 mm deep cavity and wall thickness of 1/2 mm. Cathode: 1/8 in dia. graphite 1 in long and pointed.	Concentration range	8 — 100%
Excitation source	250 volts DC 17 amperes		
Analytical gap	4 mm		
Emulsion	Eastman spectrum analysis No. 1		

The adverse effects of variations in the effective excitation temperature occasioned by any of the processes previously mentioned can be minimized or even eliminated by selecting a line pair with similar excitation characteristics. The logical approach to this selection is to utilize the excitation potential data in the spectroscopic literature.[22] This data was presented earlier for the Y/Ce line pair; quantitative data for the Gd/Ce line pairs were not available. The effectiveness of a line pair in minimizing the effects of excitation temperature variations may be determined by systematically changing the externally controllable variables whose primary or secondary effects produce significant changes in the excitation conditions. Figure 5 summarizes the results from such a study with the line pairs used in this method. Even though large changes in the individual line intensities are instituted by the changes in arc current, weight of charge, and per cent graphite, and smaller changes by the other variables, the effect on the intensity ratios is negligible. Besides verifying the homologous nature of the line pairs, these results also indicate the wide range of experimental conditions under which reproducibility is maintained.

Dieke[23] has pointed out that since excitation is not uniform along the length of the arc discharge, the excitation characteristics of a line pair may be compared by observation of the arc column along the longitudinal axis. Most of the voltage drop occurs within the electronic free path of the cathode, consequently an enhancement of the spectra which arise in higher energy states and in singly or doubly ionized ionized atoms occurs near the cathode. Therefore the change in line intensity and intensity ratio under large differences of excitation conditions can be observed by focusing the arc on the slit of a stigmatic spectrograph. Figures 6 and 7 illustrate the diagrams obtained when the spectra were photographed under those conditions. The diagrams clearly show the 3- to 4-fold parallel increase in intensity of the individual line intensities near the cathode, while the intensity ratios show only a strikingly small change. No significant change in the shape of these curves was noted when the samples were arced at 10 amperes rather than the usual 17 amperes. This verified the high degree of current independence of the intensity
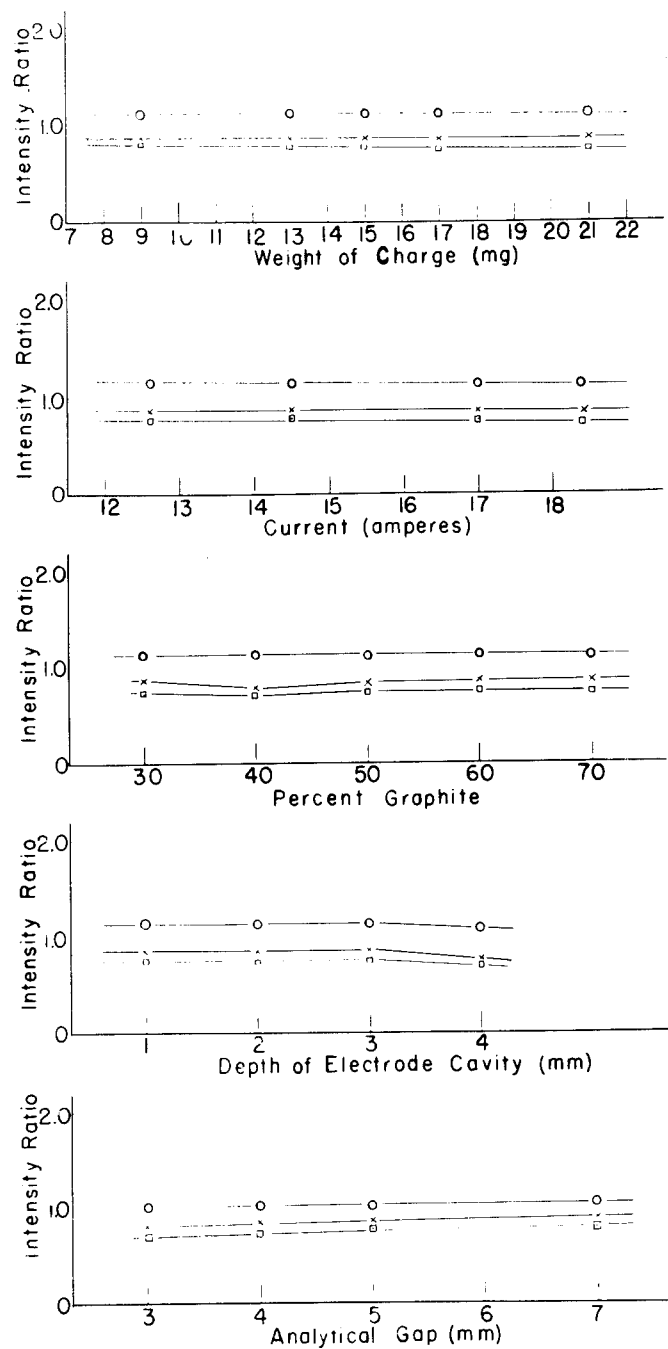
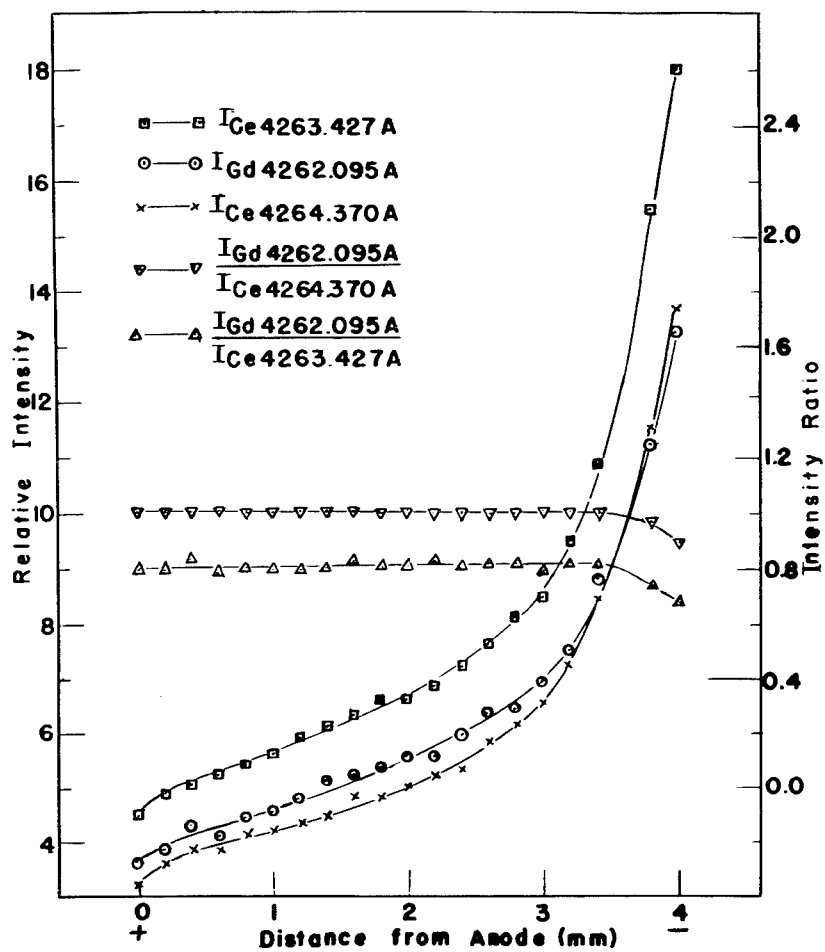Figure 5. Effect of changes in excitation conditions on analytical intensity ratios.

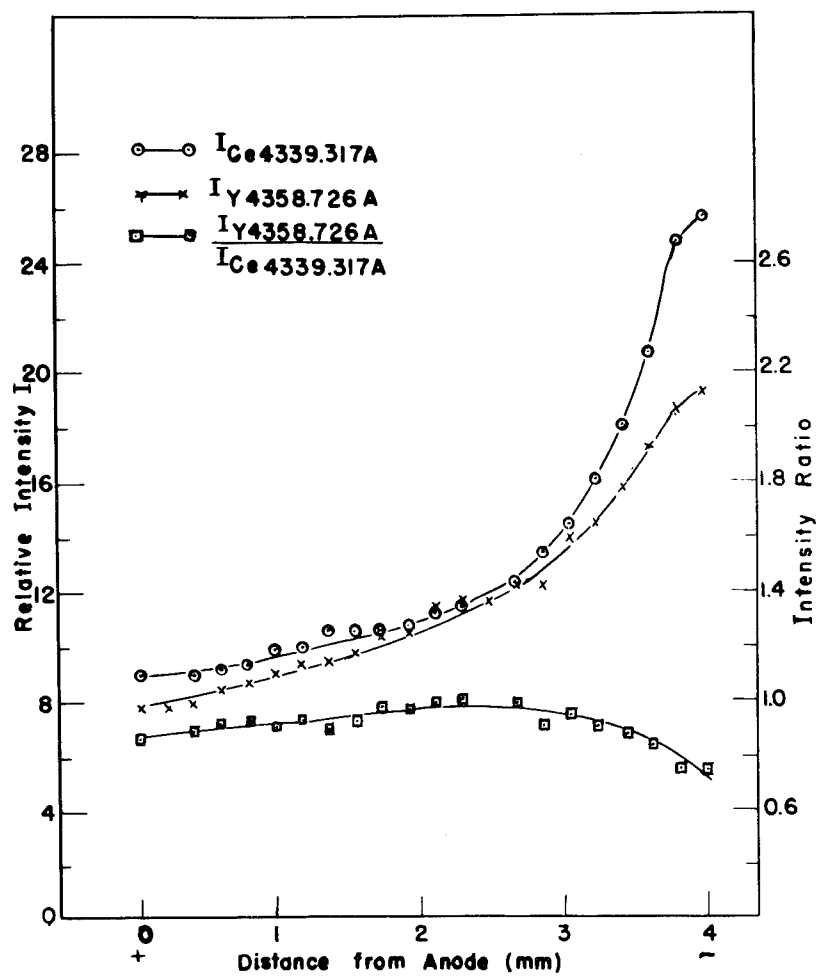Figure 6. Intensity diagrams for line pairs used for the determination of gadolinium.

Figure 7. Intensity diagrams for line pair used for the determination of yttrium.

Table 4. Comparative spectrographic and atomic weight method analyses.

Sample number	% Y_2O_3 (spectrographic)	% Y_2O_3 (atomic weight)
1	92.5	90.5
2	82.5	81.8
3	87.0	84.5

individual line intensities, whereas the intensity ratio would undergo only a negligible change. This emphasizes one of the virtues of the internal standard principle when proper line pairs are utilized.

The data presented above verify the well-known thesis that if proper emphasis is placed on satisfying the essential criteria of the internal standard principle the nonreproducibility of DC arc excitation can be overcome.

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