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Quantitative spectrographic analysis of hafnium-zirconium mixtures

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QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF HAFNIUM-ZIRCONIUM MIXTURES

by

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I. INTRODUCTION

In general, the analysis of mixtures of chemically similar elements by traditional analytical procedures is a difficult, if not impossible, task. For example, the rare earth elements are chemically so similar that the usual gravimetric methods of analytical chemistry (with the exception of a few whose anomalous valence permit a gravimetric separation) serve to determine only total rare earths.

The analysis of mixtures of zirconium and hafnium is another example where ordinary analytical methods have thus far failed completely. This failure is quite understandable, for the elements are so similar that no reagent will quantitatively separate one from the other. Indeed, all chemical procedures (except for atomic weight methods) for determining zirconium imply, tacitly or otherwise, that the method actually determines zirconium along with any hafnium which is present.

The techniques of emission spectroscopy offer a particularly good solution to the problem of analyzing such mixtures. Since the emission spectra of an element are independent of its chemical properties, analytical methods based on such spectra are unaffected by chemical similarities. In fact, as will be pointed out later, such systems are almost ideally suitable for analysis by spectrochemical methods.

Spectrochemical determinations are generally considered valid only for the determination of minor constituents. It will be shown, however, that in the case of hafnium-zirconium mixtures not only may small amounts of hafnium in zirconium be determined and vice versa, but that high concentrations of one in the other may also be analyzed. The successful analysis of the latter will be shown to depend upon: (a) the employment of an excitation source which may be rigidly controlled and which inherently minimizes extraneous influences and reversal effects, (b) the careful choice of internal standard line pairs, and (c) certain refinements in the photographic technique.

II. SURVEY OF METHODS FOR THE ANALYSIS OF HAFNIUM-ZIRCONIUM MIXTURES

The analysis of hafnium-zirconium mixtures has, in general, been of limited interest to the analytical chemist. Hafnium, because of its similar chemical properties, is assumed to accompany zirconium in all procedures which deal with the separation and the determination of the latter (1). The discussion given below is a survey of the methods which have been employed by various workers in attacking this problem.

A. Chemical Methods

Reference was previously made to the fact that these two elements are very similar in chemical properties. Hafnium is somewhat more basic than zirconium and its salts have a slightly different solubility. These differences are so small, however, that chemical methods of separation which depend upon them are not quantitative.

It might be presumed that any chemical procedure for the analysis of a mixture of these two elements would be one in the nature of an atomic weight determination. One such procedure is found in the literature (2), and it has been of value to workers in following fractionations.

The basis of the so-called selenite method lies in the discovery by Claasen (2) that both hafnium and zirconium form basic selenites upon a reaction of the oxychloride with excess selenious acid. After long digestion with excess acid, the basic selenites are converted to normal selenites. These are crystalline compounds of definite composition and may be weighed as such. After weighing, the selenite may be ignited to the oxide, which in turn may be weighed again. The percentage of hafnium (as hafnium oxide) may be found:

$$\%HfO_2 = \frac{374.86\ [\text{wt. oxides} - .35702\ (\text{wt. selenites})]}{\text{wt. oxides}}$$

While this procedure is one of the better methods of analyzing mixtures of hafnium and zirconium, it is time-consuming, and its accuracy falls off when determining small amounts of hafnium in zirconium and vice versa. It is essential that the basic selenite be digested for a sufficient length of time (12-15 hours) to be converted quantitatively into the normal selenite. Furthermore, since a pure binary mixture is needed, a preliminary purification is necessary. When the hafnium concentration is 25%, the accuracy of the method is ±0.5% (3).

B. Physical Methods

1. Density determinations

One striking difference in the properties of these two elements is in the density of their respective oxides. Since the density of ZrO_2 is 6.13 and that of HfO_2 is 10.47 (4), a density determination of the mixed oxides is a measure of composition.

The expression for per cent hafnium oxide is

$$\%\ HfO_2 = \frac{\rho_{mixture} - \rho_{ZrO_2}}{\rho_{HfO_2} - \rho_{ZrO_2}} \times \frac{\rho_{HfO_2}}{\rho_{mixture}}$$

While this method has been widely used in the past to follow fractionations, it has many limitations. The oxides must be thoroughly de-gassed before a density determination can be made. Since different crystal structures are formed at different temperatures (4), the conditions of the ignition influence the density of the oxides and must be carefully controlled. It has the same disadvantages as the selenite method in that a pure binary mixture must be used, and in that its accuracy decreases as the concentration of either oxide increases. Larsen, Fernelius, and Quill (5) have compared the results obtained by this method with that obtained by the selenite method. The following are some examples:

% Hf by density	% Hf by selenite
23.2	23.6
50.4	51.0
87.8	93.3
89.0	97.7

It will be noted that the methods are in fair agreement except at high hafnium concentrations where both methods have a large error.

2. X-ray emission spectra

Since von Hevesy's discovery of hafnium, X-ray emission spectroscopy has played an important role in its analytical chemistry (6). It was by this method that von Hevesy followed fractional precipitation procedures which enabled him to prepare pure hafnium oxide. Kimura (7) has shown that by using the $L\beta_1$ line of hafnium together with the $L\beta_1$ line of lutetium as an internal standard he could determine the percentage of hafnium in mixtures of phosphates and oxides of hafnium and zirconium. This method has the disadvantages of a lack of sensitivity and of the difficulty of measuring the blackening of an X-ray film. Furthermore, since the sample must be deposited on the anode of the X-ray tube itself, the method is inconvenient to use.

3. Optical rotation

It has been found (8) that zirconium had somewhat less effect than hafnium oxychloride on the amount of rotation which tartaric acid solutions imparted to plane polarized light. Wernimont and De Vries (9) showed that this could be made the basis of an analytical procedure. Preliminary studies by these workers showed that a comparison of analytical results by this method was within ±10% of the values obtained from density determinations. It has the same disadvantages of the selenite and density methods in that pure binary mixtures are necessary and it is not sensitive at low concentrations of hafnium in zirconium and vice versa.

4. Radiochemical

If a mixture of hafnium and zirconium is irradiated with slow neutrons, two hafnium isotopes are formed, one with a 19-20 second half-life (10, 11), the other having a 45-55 day activity (10). Either of these activities may be counted and the hafnium content determined. The error is in the order of 10%.

The fact that the neutron capture cross-section of hafnium is much greater than that of zirconium (12) is the basis for another radiochemical method which has been used as an analytical tool. The Hf/Zr ratio may be found if the neutron capture cross-section of the unknown sample is determined and corrections applied for the capture cross-section of any other impurities in the sample.

In general, these methods are of academic interest only and are of little value as a practical analytical method.

5. Optical emission spectra

In view of the revived interest in the separation of hafnium and zirconium, it is not surprising that spectrographic methods have been proposed for the analysis of these mixtures. Feldman (10) has shown that the porous cup technique (13) may be used for the analysis of solutions of hafnium and zirconium. While this technique has the advantage that solutions may be analyzed directly, it is also limited in the same respect. Some zirconium compounds, notably the oxide and the pyrophosphate, are difficult to dissolve and the extra operations involved in fusing such a sample, followed by chemical separation from the fusing agent, restrict the porous cup technique.

While the present investigation was in progress, Chandler (14) reported on a method for determining high hafnium concentrations. Chandler measured the intensity ratio of HfII 2638.710/ZrI 2640.5 for samples containing 1.0-50.0 per cent hafnium. In order to determine higher concentrations of hafnium, the sample was diluted 1:1 with pure zirconium oxide and the same line pair ratio was measured.

The successful use of the type of excitation which Chandler used (a d. c. arc) was apparently dependent upon a carefully controlled method of preparing the sample. The oxide was prepared from the selenite by the ignition of the latter under controlled conditions. In order to use this method on a sample of zirconium oxide or phosphate, it would be necessary to fuse the sample, carry out a double precipitation of the hydroxide to remove the excess alkali metal ion, precipitate the basic selenite, digest the latter to form the normal selenite, filter, wash and ignite to the oxide. Obviously this method of sample preparation is quite involved.

Chandler's choice of line pair seems to be particularly unfortunate in several respects. The excitation potentials of the lines differ by a factor of two (10.2 electron volts vs. 4.7 electron volts), and this gives rise to erratic results in any type discharge. The HfII 2638.710 is a resonance line of the HfII spectra and has a tendency to exhibit self-absorption. The self-absorption would become particularly pronounced at the high hafnium concentration for which the method is used. Furthermore, the HfII line has a fairly serious interference in the TiII 2638.705 as well as in a weak line of zirconium (2638.714).

The method for extending the working curve for higher concentration of hafnium, i.e., dilution of the sample, has the obvious limitation that any errors are magnified when the dilution factor is taken into account. In analyzing high hafnium concentrations the error could easily be 10% of the amount present.

Other spectrochemical methods for determining Hf/Zr ratios have been described (15,16), but these were only semi-quantitative in nature and no detailed procedures were given.

III. THE DETERMINATION OF MAJOR CONSTITUENTS BY SPECTROGRAPHIC METHODS

A. Historical

Generally speaking, spectrochemical methods until recently have been considered to be valid only in analyzing for minor impurities. Indeed, a recent book on spectroscopy states (17):

> The upper limit of concentration at which ordinary methods become uncertain is usually given as 5 per cent, although in some cases 10 per cent concentration can be reached when only one variable is involved.

In the past two years there have been a number of articles published on the spectrochemical determination of constituents at higher concentrations. Probably the outstanding application in this respect has been in the analysis of high-alloy steels (18). It has been shown that spectrographic methods can determine alloying constituents with an accuracy which competes with routine chemical methods. Such precise results have been shown to depend upon (a) rigidly controlled excitation such that the influence of one element upon another is eliminated, (b) the use of direct reading methods for measuring spectral intensities, i.e., measuring light intensities electronically, and (c) the development of rigorous calculating methods.

High cobalt alloys have been analyzed spectrographically for higher percentages of molybdenum, manganese, iron, chromium, silicon, and nickel by Sihvonen and co-workers (19). These workers reported a precision of 3.7-11.17 per cent and an accuracy of 3.5-10.3 per cent.

Spectrographic methods have also been successfully applied to determination of constituents up to 100 per cent. Fassel (20), using a d.c. arc as an excitation source, analyzed yttrium and gadolinium as major constituents in mixtures of other rare earth oxides. Fassel obtained a high degree of precision -- a per cent standard deviation of $\pm 2.5\%$ -- for the type of discharge which was employed. The high precision obtained was attributed to the high degree in which the chosen internal standard compensated for the excitation variables. Herman (21) has shown that binary mixtures of niobium and tantalum may be analyzed spectrographically. Herman claimed that the accuracy was within one unit per cent of the actual value when the average of three exposures was used. Chandler's work on the analysis of hafnium and zirconium has been reviewed previously (p. 8).

One of the reasons that there has been little work done on the determination of higher concentrations of elements is probably due to the fact that there are several problems which become more serious when the analysis for a major constituent is desired. These difficulties are listed below and will be discussed further under separate headings.

1. Self-absorption must be eliminated or minimized.
2. The influence that one element exerts upon the intensity of lines of another element must be minimized.
3. Experimental errors assume a greater significance. These may be divided into excitation and photometric errors. The former may be reduced by the proper choice of controlled excitation conditions. The latter are minimized by means of refinements in photometry.

B. Theoretical

If an atom is excited by thermal, electrical, or radiant energy, the electrons are raised into higher energy states. When an electron returns to a lower state, its energy is lost through radiation or transferred by collision with another another atom. The energy which is emitted in the form of radiant energy and the wave-length of the light are related by the following expression:

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

where E = energy emitted

E_2 = total energy of the higher state

E_1 = total energy of the lower state

h = Planck's constant

ν = frequency of emitted light

c = velocity of light

λ = wave-length of emitted light

Much theoretical and experimental work has been done on the analysis of the spectra, and for a complete discussion of this subject one must consult specialized treatises (22). As a result of this work, it has been shown that the emission and absorption of energy takes place according to definite rules. The excitation of electrons may take place in such a manner that the electrons may occupy only certain predetermined energy states, and furthermore, the electrons may return to their lowest level only in finite steps. For example, an electron may go from an excited state to the lowest or ground state in one step, or it may go from the excited state to an intermediate state in one step, then to the ground state in another step.

There are many possible values of energy states and energy levels, each of which is a characteristic of a given kind of atom. The wave-lengths of the light emitted are likewise characteristic of the atom.

If these wave-lengths are dispersed by a spectrograph or spectroscope, the distribution of these wave-lengths gives rise to the characteristic spectrum of the element. This spectrum may then be used for the qualitative identification of the element.

The basis of quantitative spectrochemical analysis lies in a correlation of line intensities with concentration. The intensity of a spectral line can be shown to be dependent upon the number of atoms which are in an excited state and the probability that the excited atom returns to a specific lower state to give rise to the spectral line (its transition probability). That the excitation of atoms in electrical excitation sources is, for the most part, a thermal phenomenon will be discussed later. If this premise is accepted, the number of atoms in an excited state, n, can be expressed:

$$N_n \propto g_n e^{-\frac{\Delta E_n}{kT}}$$

Where N_n = number of atoms in excited state n

g_n = statistical weight factor

ΔE_n = energy above the ground state

k = Boltzmann constant

T = absolute temperature

The expression for the intensity of a line arising from state n is:

$$I_n \propto P_n g_n e^{-\frac{\Delta E_n}{kT}}$$

Where P_n = transition probability

I_n = intensity of line

Consider the ratio of intensities of two lines of the same element, one arising from a state n, the other from state m. Then,

$$\frac{I_n}{I_m} \propto \frac{P_n g_n e^{-\frac{\Delta E_n}{KT}}}{P_m g_n e^{-\frac{\Delta E_m}{KT}}}$$

In ordinary laboratory excitation sources, the transition probabilities P_n and P_m may be assumed constant. Then,

$$\frac{I_n}{I_m} = Ke^{\frac{\Delta E_m - \Delta E_n}{KT}}$$

If two different elements, A and B, are in a discharge, a similar expression is valid if the appropriate concentration terms are inserted.

$$\frac{I_A}{I_B} = Ke^{\frac{\Delta E_B - \Delta E_A}{KT}} \cdot \frac{C_A}{C_B}$$

It is evident from this equation that the ratio of intensities is dependent upon the temperature of excitation, as well as concentration ratio. Since in actual practice it is difficult to control the temperature precisely, another means must be used to obtain a constant relationship between intensity ratio and concentration ratio. It will be noted in the equation above that if the exponential term is zero, i.e. when $\Delta E_A = \Delta E_B$, the expression is no longer dependent upon temperature. Hence, if lines are chosen which have similar excitation potentials, fluctuations in excitation will have little effect on intensity ratio. On the other hand, lines which have substantially different excitation potentials should show widespread fluctuations under different discharge conditions. Experiments verifying these conclusions will be discussed in a later section.

If equal excitation potentials or a controlled excitation temperature is assumed the following relationship between intensity ratio and concentration is obtained:

$$\frac{I_A}{I_B} = k \frac{C_A}{C_B}$$

Thus far, the ideal case, in which no self-absorption occurred in the discharge, has been considered. In order to allow for the presence of this effect, an exponential term should be included in this expression. Then,

$$\frac{I_A}{I_B} = k\left(\frac{C_A}{C_B}\right)^n$$

Since

$$\log \frac{I_A}{I_B} = n \log \frac{C_A}{C_B} + \log k$$

a plot of log intensity ratio against log concentration ratio results in a straight line of slope n. When no self-absorption takes place the slope is one.

Throughout this discussion, it has been tacitly assumed that the ratio of concentration of elements A and B in the discharge vapor was the same as in the electrode. It is fortunate that chemically similar elements often possess similar physical properties and volatilize at the same rate. It will be shown later that hafnium and zirconium, for example, have identical distillation rates.

The above discussion is the basis for the internal standard method of spectrochemical analysis. This technique was introduced by Gerlach and Schweitzer (23) and is now almost universally used in quantitative work. This procedure involves the use of either (a) a line of the matrix material which is known to be constant in its intensity, or (b) a line of an element which is known to be absent in the sample, and which is introduced in a known constant amount. As was pointed out earlier, a ratio of the unknown constituent line to the internal standard line is a measure of the amount of unknown present. The proper use of this method tends to cancel out variables in photometry as well as in excitation.

C. Problem of Self-absorption

Radiant energy which is emitted by an excited atom may be reabsorbed in the cool vapor surrounding the exciting source. The net result of this process is that the amount of light of a given wave-length falling on a photographic plate will not be proportional to the amount emitted by the excited atom. This type of absorption is termed self-absorption and may be compared to the familiar Fraunhofer lines of the solar spectrum. In the latter case the light given off by the excited atoms is completely absorbed by the cool vapor surrounding the sun.

In spectroscopy, self-absorption is sometimes called self-reversal, because the spectral line appears on a photographic plate as a broadened line with its center sharply cut out, or, if the spectrograph is of moderate resolution, the line will appear diminished in its intensity.

The mechanism of self-reversal is fairly well understood. Since the population of the lowest, or ground state, of the atom is relatively large in the cool vapor surrounding the discharge, there will be a tendency for that line whose lowest state is the ground state to be absorbed. While it is true that there can be atoms in states other than the ground state in the cool vapor, and that lines falling to other states may be absorbed, the number of atoms in these higher states diminish quite rapidly as the energy increases. Langstroth (24) has estimated the relative population of the $3s^2S_{1/2}$ state (the ground level) of MgI to be 1000 while the $3p^2P^o_{3/2}$ (a higher level) is estimated to be 0.3.

The ensuing discussion of self-absorption follows that described by Dieke (25). The treatment given is fairly simple but is adequate for our purposes. Let the line be emitted at the center of the light source with intensity I_o and traverse an optical path of length L.

Then,

$$L = \int N_r dr$$

where N_r is the number of atoms per unit volume at distance r from the light source which are capable of absorbing the particular line, i.e., atoms which are in the lower state of the emission line.

The intensity of light far from the light source, i.e., outside the region of self-absorption, is then

$$I = I_o e^{-aL}$$

where a is the absorption coefficient per unit number of atoms which absorb. Since this coefficient is proportional to the transition probability which in turn is proportional to I_o,

$$a = \alpha I_o$$

and for a limited wave-length region may be considered constant,

$$I = I_0 e^{-\alpha L I_0}$$

$$\text{and } \log I/I_0 = -\alpha L I_0$$

$$\text{if } x = \log I_0, \quad e^x = I_0, \text{ and}$$

$$\log I/I_0 = -\alpha L e^x$$

Dieke has measured I and I_0 for iron lines. In measuring I_0, he used carbon electrodes containing iron as an impurity so that the absorbing cloud would be at a minimum. He found that in some cases $\log I/I_0 = 2$. This means that 99 per cent of the light of those lines was lost by the self-reversal process.

In analyzing trace quantities of elements, the problem of self-reversal need not be considered seriously, since the amount of the element in the cold vapor is very small. Indeed, it is fortunate that such is the case, for the most sensitive lines of the elements are those which arise from transitions to the ground state.

If, however, one wishes to analyze quantitatively for higher concentrations of elements this problem merits serious attention. Since the amount of absorption is dependent upon the density of the element in the cool vapor surrounding the discharge, any variable influencing this density, (in particular, the air currents in the discharge and the temperature of the discharge) will affect the amount of absorption. Since it is particularly difficult to control these varibles -- it has been claimed that an opened door or the breathing of the observer influences the absorption (25) -- the use of lines subject to this phenomenon is quite objectionable.

In order to overcome this objection, it is necessary to choose lines in which self-reversal, if it is not entirely eliminated, is reduced to a minimum. It is fortunate that the theoretical work which has been done on the classification of the spectra of many elements is helpful in the selection of such lines. Through the spectral classification one is able to choose only those lines whose lower state is not the ground level; hence these lines are much less susceptible to self-reversal. The intensity of these lines then remain proportional to the concentration of atoms.

It follows from the previous discussion that the choice of lines to be used for the analysis of high concentrations is limited to those whose lower state is at a relatively high energy level. In order to obtain these higher energy levels it is necessary to employ a relatively high-energy source of excitation. It will be pointed out later that an over-damped condenser discharge is admirably suited for such type of excitation.

D. Effect of Extraneous Materials

That the internal standard technique was an important advancement in spectrographic analysis has been demonstrated in previous discussions. Ideally, the internal standard element compensates for all variations in excitation and photometry. Practically, however, the best an internal standard can do is to minimize these variables. Its use depends upon the assumption that at a fixed concentration of unknown element, the ratio of the intensity of the line of the unknown element to the intensity of the internal standard is essentially constant. This relationship does not hold, in general, when additional elements, so-called extraneous elements, are present in the sample. As a result, the ratio of line pair intensities is a function of the amount and kind of extraneous elements present. The importance of this effect in quantitative work is to limit spectrographic analysis to samples which have very nearly the same chemical composition as the standard samples upon which the working curve is based.

Many workers have observed the extraneous effect, and much attention has been given to its causes and correlations. Fast (26) gives a review of the literature on this subject, and it will not be repeated here. Investigations by some Russian workers have been discussed by Smith (27) and will be reviewed briefly from a fundamental viewpoint.

These investigations, by Mandel'shtam (28), and Khramova (29), have confirmed the fact which spectroscopists had long suspected, that the excitation of spectra, whether by flame, arc or spark, is a thermal phenomenon. The former investigated the intensities of lines as a function of temperature, and found them to increase to a maximum, then decrease as the temperature was raised. Ornstein (30) then showed that a carbon arc which burns in an atmosphere of sodium (as sodium chloride) is at a lower temperature than an ordinary arc.

As a result of this evidence, these workers explain the extraneous effect as an effect which results from the lowering of the excitation temperature by the presence of easy ionizable components. Langstroth and Newbound (31), on the contrary, in their work on the effect of extraneous materials on magnesium, cadmium and lead intensity ratios, found it difficult to correlate the intensity variations with effective temperature. It might be pointed out that in the latter case, resonance lines were used almost exclusively. The use of these lines is objectionable in that the intensities of these lines are dependent not only upon temperature of excitation, but also upon the amount of self-absorption which takes place.

It has been found that the effect of extraneous materials can be reduced by the use of buffers or by choosing the proper excitation conditions. It will be shown that this effect was minimized in this investigation through the use of the latter technique, together with the choice of an internal standard whose excitation and volatilization characteristics closely paralleled that of the unknown.

E. Excitation

The proper excitation of the sample is a subject which has received much attention from spectrographers in the past few years. The importance of this subject has arisen from statistical studies made by Grossman, Sawyer and Vincent (32) on the errors associated with spectrochemical analysis. They found that they could attribute the greatest source of error to the excitation of the sample even when employing a controlled spark discharge. While their studies were made on steel samples, there is little doubt that their conclusions are of universal application. In recognizing this source of error, Scribner (33) states:

> It has become evident that the future development of spectrographic analysis will depend largely on improvements in present excitation sources.

It is clear that a spectrographic (excitation) source fulfills two purposes. First, it causes the vaporization and the dissociation of the sample, and second, it is the means of exciting the atoms so that they may emit their characteristic radiation. Hence, the problems of obtaining a reproducible source depends upon a controlled vaporization as well as a controlled excitation.

1. D. C. arc sources

The use of an electric arc is a quite common practice in emission spectroscopy because it possesses advantages of simplicity and sensitivity which are difficult to duplicate. Its only requirements are a d.c. power source, usually 220 volts, and a ballast resistance. It has been found satisfactory for use with a wide range of base materials. Unfortunately, the d.c. arc is erratic in its behavior and the reproducibility of spectral lines obtained from this source is poor.

Many workers have attempted to overcome these objections by various devices. Vincent and Sawyer (34) stabilized the arc considerably by rotating the lower electrode at about 600 revolutions per minute. A rotating magnet (35) as well as a magnetic field (36) has been used to stabilize the discharge.

Probably the most satisfactory means of reducing the light source fluctuation and its effects is through the use of various buffers and through the judicious choice of an internal standard. Strock (37) has pointed out that progress has been made in applying d.c. arc methods to the analysis of refractory materials only through the use of these methods. He points out that a small sample placed in an arc crater behaves very similarly as would a larger bulk placed in a metallurgical furnace. He further shows that the fractional distillation effects can be made a more gradual process when a suitable buffer, e.g., graphite powder, is used. If the internal standard which is chosen possesses a similar volatility as the unknown material and has similar excitation characteristics, it is possible to compensate for the erratic behavior of the d.c. arc. As was pointed out earlier, Fassel (20) obtained a high degree of precision by means of an internal standard which exhibited almost an ideal behavior.

It will be pointed out later that preliminary experiments indicated that the d.c. arc was inadequate for high precision analysis of zirconium.

2. Spark sources

Earlier investigators soon realized that an alternating current spark excitation would be somewhat more controllable than the d.c. arc. Meggers (38), for example, in his classic paper demonstrating the feasibility of spectrographic analysis, used this type of excitation.

At present a large share of the quantitative analysis of metals is accomplished by means of a.c. spark sources (39). In earlier work an uncontrolled, or free-running spark, was used. A typical example of such a spark consisted essentially of a 10,000 to 40,000 volt transformer, a capacitance of 0.002

to 0.02 microfarad, an inductance of a few hundredths of a millihenry, and a resistance of a few ohms. The analytical gap, the self-inductance, and the resistance were used in series across the secondary of the transformer with the capacitance connected in parallel with the gap.

One difficulty observed with this source was the inability to obtain a reproducible break-down potential of the gap. This in turn affected the stability of the source and resulted in a lack of precision in the spectrographic results. In order to overcome this defect, Feussner (40) proposed the use of a so-called controlled condensed spark discharge. In this type of circuit a rotatory interruptor which is operated by a synchronous motor controls the sparking potential so that the discharge takes place only when the condenser is at peak voltage.

Vincent and Sawyer (34) have simplified the original Feussner circuit and this circuit is shown in Figure 1. The transformer charges the condenser C which is discharged at the proper moment by the synchronous gap. The discharge then takes place through the resistor R., inductance L, and the analysis gap G. The peak voltage is 40,000 volts, and the circuit constants R, L, and C may be adjusted to give different types of discharge.

While the excitation sources which have been described thus far have found widespread use in modern spectrographic

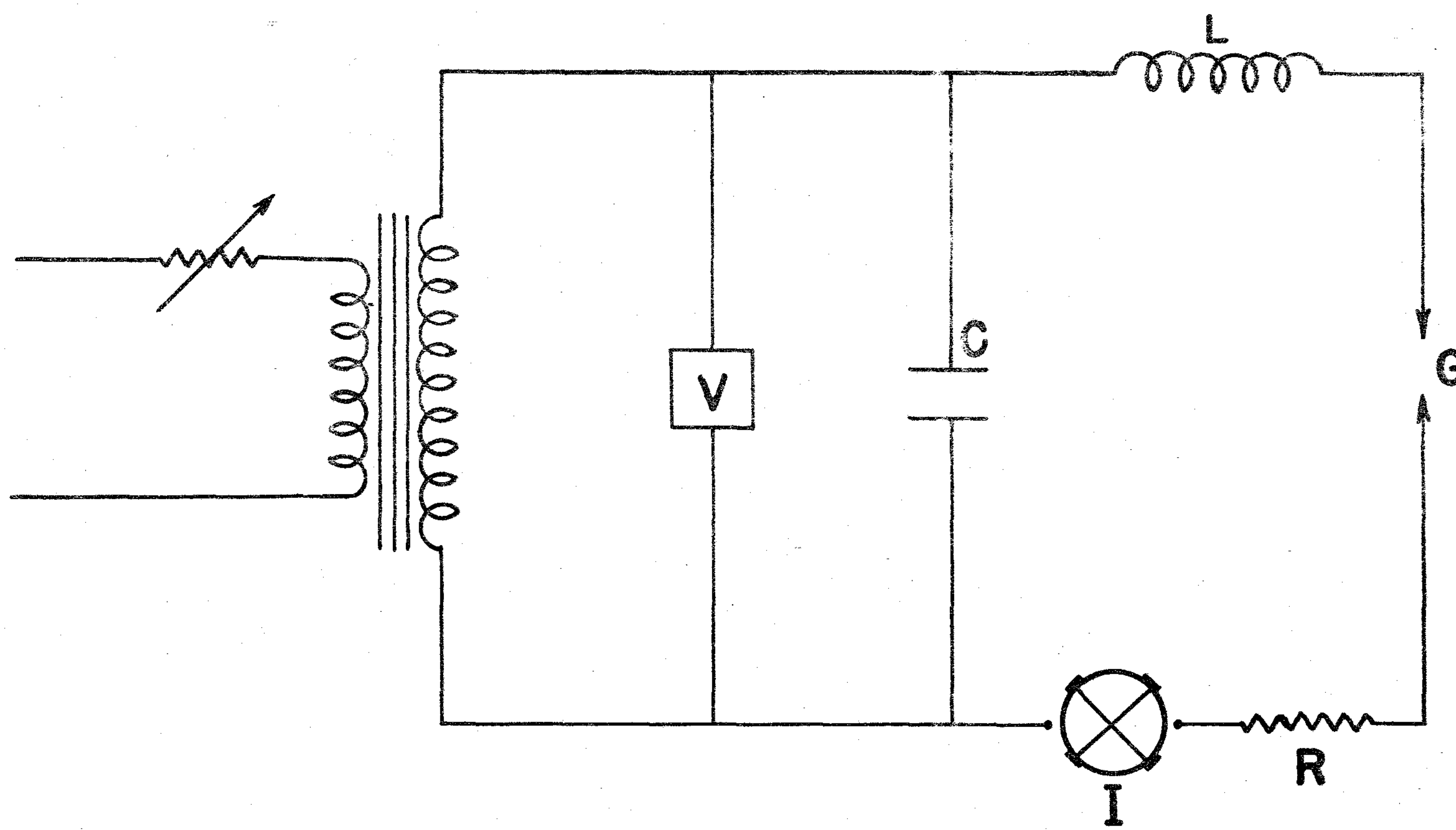

Figure 1. Controlled Spark Circuit

laboratories, they fail to provide certain refinements which sould be desirable.

The spark sources thus far considered have the following shortcomings:

1. Their use results in a lack of sensitivity of the spectrographic method.

2. They fail to provide for means of employing very high values of capacitance so that an overdamped discharge may be obtained. This type of discharge possesses a long time constant and passes large amounts of energy through the analytical gap.

3. They do not provide sufficient flexibility in the type of excitation which may be obtained.

3. The multisource unit

Hasler and Dietert (41) recognized these limitations and have described an excitation source, termed a multisource unit, which was designed to correct them.

The basic circuit is shown in Figure 2. It is composed essentially of two parts, a high voltage ignitor circuit and a low voltage power circuit. During the charging cycle, the power condenser -- also the ignitor condenser -- is charged to a definite peak voltage. The ignitor circuit initiates the discharge at a selected time during either the charging or discharging period. The time of initiation is regulated by means of the synchronous gap, and can be adjusted with great precision. After the analytical gap has been broken down by the ignitor circuit, the large condenser bank dis-

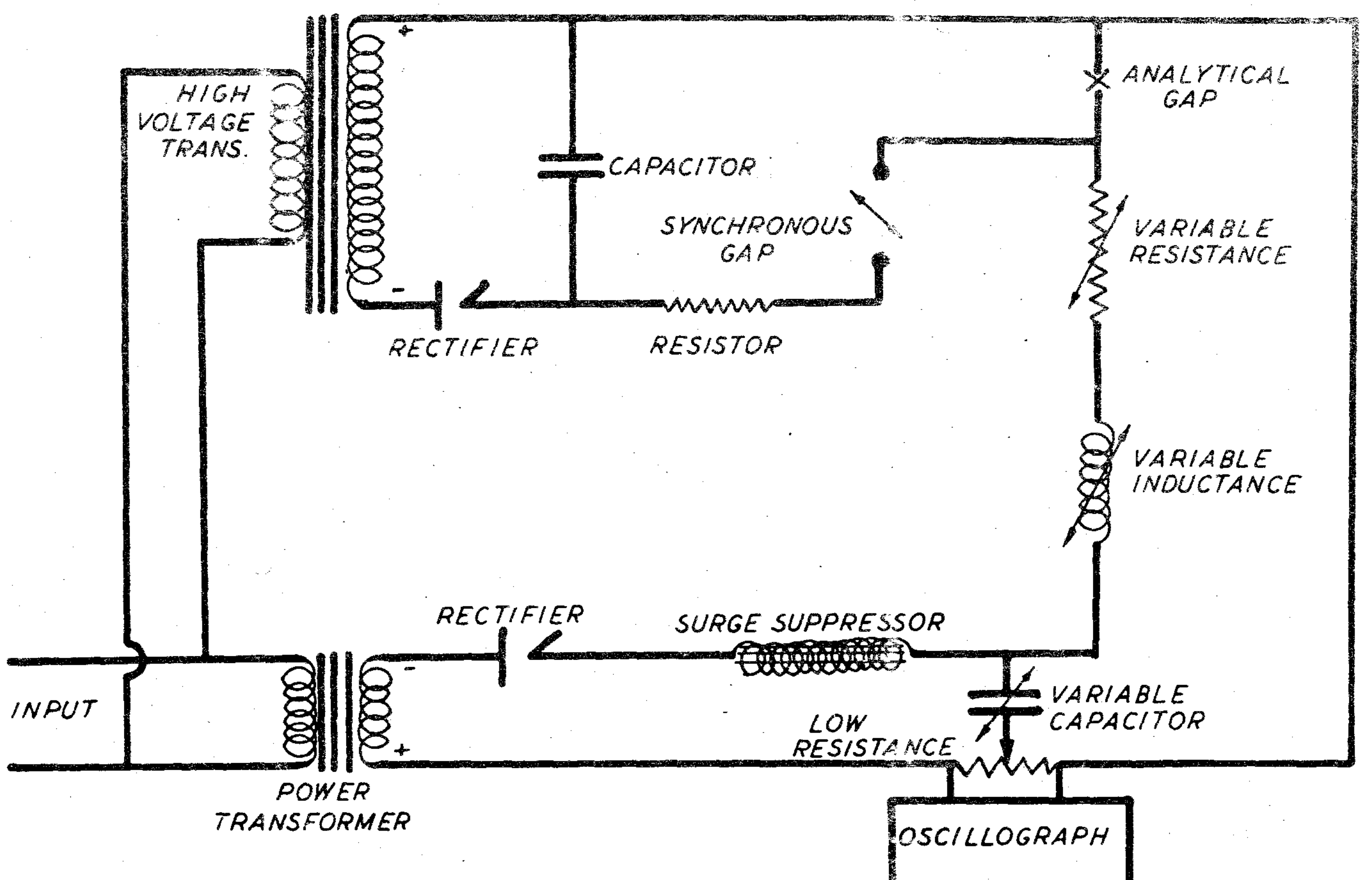

Figure 2. Basic Circuit of Multisource Unit

charges through a power resistor, inductance, and the analytical gap. Since the inductance and resistance may be varied as well as the capacitance, wide, controlled variations may be obtained with this source unit. A built-in oscillographic unit illustrates the wave form of the discharge and charge currents.

Hasler and Dietert (41) show that there is a complete separation of the charge and the discharge current, if the ignition takes place after the condenser is charged, and further show that the discharge is independent of the low powered ignitor circuit. Thus it is evident that if means are available for controlling the peak voltage to which the power condenser is charged, exact equality of discharges should occur. These workers have also found that the proper choice of circuit constants has a stabilizing influence on the discharge.

It would be expected that the precision which is attainable with this source unit would be very high. This has been found to be true, for it is by the use of such an excitation source (together with electronic methods of measuring light intensities) that the error in analyzing ferrous materials is approximately $\pm 0.3\%$ (18).

The fact that very high values of capacitance may be employed is of interest from several viewpoints. As was mentioned previously, this allows the use of an overdamped discharge which passes large amounts of energy through the analytical gap. This is of interest in the case of the excitation of refractory materials where the vaporization of the sample is particularly difficult. Herdle and Wolthorn (42) have used this type of discharge successfully in the analysis of silica refractories for various impurities. Helz and Scribner (43) also found this type of discharge to be useful in the analysis of portland cement.

The use of an overdamped condenser discharge has been shown to result in a minimum of self-reversal effects if the proper line pair is chosen. By the proper choice of source constants a discharge may be obtained which excites lines which start and end in high energy states. It has been pointed out that these lines are less susceptible to self-absorption. Hasler (41) has shown that in the case of the analysis of copper in aluminum, a linear relationship holds between intensity ratio and concentration over a two-hundred-fold variation of values. Since the slope of this function was unity, there was little or no self-absorption in this case.

The characteristics of this discharge are such that small amounts of sample are vaporized during each half cycle. Because there is a relatively large quantity of energy available for the excitation of a small amount of sample, it might be expected that the extraneous effect would be minimized. While there has been very little work done on the effect of extraneous materials in a discharge of this type, Hasler (18) believes that the successful application of spectrographic methods to the analysis of high alloy steels depends in part upon the use of such a discharge. The latter was claimed instrumental in eliminating the effect of large changes in the concentrations of the alloying elements.

F. Problem of Photometry

The photographic emulsion has in the past proved to be the most popular medium for the measurement of the radiant energy emitted by the excited atoms. Although the recent introduction of direct reading methods (44, 45, 46, 47) has tended to supercede photographic methods where a large volume of routine analytical work must be done, the latter method will no doubt continue to be an important technique for many years. Advantages which photography possesses include its high sensitivity, its feature of integrating the light which falls on the emulsion over the entire period of exposure, and its ability to record a large number of spectral lines simultaneously. It also constitutes a permanent record. It is not without its disadvantages, however, and in order to use it successfully in quantitative analysis, careful attention must be given to the control of its many variables. These variables include its non-linear response to light, its change of sensitivity and contrast with wave length, and its change of contrast with temperature and time of development.

In spite of these difficulties the photographic error can be made quite small by means of careful techniques. Kaiser (48) and Vincent and Sawyer (49) have shown that this error is much smaller than that involved in the excitation sample. These conclusions were critized by Irish (50) because Kaiser confined his study to but one plate, and Vincent and Sawyer limited their study to a few plates exposed over a short period of time. Irish claims that the photographic error is considerable when spectrograms and photographic plates are used in large quantities.

The errors associated with photographic photometry may be minimized by the proper control of several experimental conditions. By a restriction of the wave length range and through the use of a thermostatically-controlled developing machine (51), the errors arising from these factors may be reduced to a negligible quantity. The use of an internal standard compensates for any residual errors from such sources.

The problem of determining the plate response to radiant energy is one which merits careful attention. Harrison (52) has reviewed the variables associated with this problem and discusses the methods available for calibrating the photographic emulsion. Sawyer and Vincent (53) have shown that the most precise methods involve either the fundamental inverse square law or the use of stepped filters. The former has the disadvantage of its lack of convenience, and the latter are difficult to prepare and calibrate.

Because of its convenience, a rotating logarithmic sector disk in front of the spectrographic slit is a widely used method of varying the light intensity by a fixed amount. Webb (54) has shown that if the sector is rotated at sufficiently high speed the intermittency effect is negligible. Lack of uniform slit illumination and non-parallelism of the slit jaws will cause errors in emulsion calibrations which have been prepared by this means. Since a short slit length may be used, the two-step method of Churchill (55) reduces such errors.

When the internal standard line has the same density as the unknown line, the errors in photometry due to the plate response are at a minimum. This may be shown by the following considerations: Over the straight portion of the plate calibration curve the following relationship is valid:

$$\log \frac{1}{T} = \gamma \log I$$

where T = per cent transmission

γ = slope of the line

I = relative intensity

Then, taking differentials,

$$d \log 1/T = \gamma \, d \log I + \log I \, d\gamma$$

$$\frac{dI}{I} = \frac{\frac{d(1/T)}{1/T} - \log I \, d\gamma}{\gamma}$$

This expression shows the relationship between the relative error in intensity, $\frac{dI}{I}$, the relative error in 1/T, the error in the emulsion calibration $d\gamma$, intensity I, and slope γ.

If we assume the following values,

$$\frac{d(1/T)}{1/T} = +0.01$$

$$I = 2.0; \log I = 1.31$$

$$\gamma = 2.0$$

$$d\gamma = -0.2$$

the relative error in intensity is +0.13 or +13%. However, it is obvious if two lines I_A and I_B are equal in density, i.e., have the same transmittancy, the ratio of the two is unaffected by errors in γ.

Consider another case in which $I_A = 2.0$ and $I_B = 8.0$, or $I_B/I_A = 4.00$, and the other values of γ, $d\gamma$ and $\frac{d(1/T)}{1/T}$ are assumed as before. The relative error in I_A is +13%, thus $I_A = 2.26$. The relative error in I_B is +16.3%.

Then $I_B = 8.00 + 1.31 = 9.31$

and $\frac{I_B}{I_A} = 4.12$

The final error in measuring the line pair ratio is then +3%, and it can be shown that for larger ratios the error continues to increase. Furthermore, the same treatment applies to ratios less than one. Finally, it may be stated that, while the internal standard method decreases the errors in photometry, this method becomes less precise as the ratios deviate from unity. This is in agreement with the conclusions of Schmidt (56) who discusses variance in spectrochemical analysis from a different point of view.

When determining high concentrations in order to reduce the photographic error to a minimum, it is necessary to have working curves whose intensity ratios do not differ greatly from one. This necessitates the use of several line pairs, each of which is useful over a short range of concentration. In the work described herein such a plan was used.

IV. EXPERIMENTAL

A. Apparatus

Much of the apparatus employed in this research has been described (57). A 21-foot grating spectrograph, manufactured by the Jarrell-Ash Company, (Boston, Massachusetts) was used in all of the experiments. This is a fully automatic instrument having a dispersion of 5.1 A/mm in the first order spectra, 2.5 A/mm in the second order, and 1.7 A/mm in the third order.

The external optical system was designed to give uniform illumination on the slit. It employed a 10.5 cm. focal-length cylindrical quartz lens with axis vertical, placed 44 cm. from the slit, and a 50 cm. focal length quartz lens with axis horizontal, placed directly in front of the slit. Two cylindrical lenses were used, rather than a single spherical lens, in order that the light would fill the grating horizontally without exceeding it vertically. The source was 55 cm. from the slit.

The electrodes were aligned by means of a projection device described by Smith and Fassel (58).

A rotating sector of the triple sector-disk had a relative exposure ratio of 1:1.585.

The excitation stand was water-cooled following the design of Scribner and Corliss (59).

An ARL-Dietert bricquetting press (60) was used to form conducting pellets from the sample-graphite mixture. This press was capable of exerting a pressure of 15,000 pounds per square inch. It was equipped with a controlling device so that pellets could be formed at a constant pressure.

An ARL-Dietert Multisource unit described previously in this paper, was used to excite the pellets. The pellets were held in a special pellet holder.

A d.c. source was used to excite an iron arc which was used in all plate calibrations. The power source was a General Electric 5 KW compound-wound generator, powered by a General Electric 7 horsepower synchronous motor. A shunt field rheostat was used to adjust the terminal voltage. A resistance box was used to adjust the current output.

The photographic plates were processed in an ARL-Dietert developing machine (51). This machine provided a constant temperature and uniform agitation for the developing process.

An ARL-Dietert Comparator-Densitometer (61) was used to measure transmittancies of the spectral lines, and an ARL-Dietert calculating board was used to convert transmittancies to relative intensities.

B. Emulsion Calibration

A determination of the response of the photographic plate to radiant energy must be made in quantitative spectrographic analysis. Probably the most convenient method of carrying out such a calibration is by means of a rotating stepped sector. It has been shown by Webb (54) that if the sector is rotated at 3000 revolutions per minute any intermittency effect is negligible.

Since the illumination was uniform only in the central portion of the slit, a two-step method of calibration was used. This has been thoroughly described in previous work (57). Because a stroboscopic effect is observed when this method is used in conjunction with an a.c. discharge, it may not be used with such an excitation source. In the calibration of all plates used in this work, a d.c. iron arc drawing 4.4 amperes was used as the light source.

The preparation of a preliminary curve is advantageous in that it smooths out the fluctuations in the densitometer readings. It was prepared in the following manner: The iron arc was exposed through two steps of a rotating stepped sector and the per cent transmissions of iron lines in the desired wave length region were measured in both steps. Thus, the intensity ratio of a particular iron line in one step to that of the same line in the other step was 1:1.585. Several (12-15) lines were measured over a wide range of transmittancy and the per cent transmission of one step was plotted against that for the other step on two-cycle logarithmic paper. A smooth curve drawn through these points constituted the preliminary curve. A typical example is shown in Figure 3.

The final emulsion calibration curve was obtained by selecting as an ordinate a per cent transmission higher than any which occurred in the experimental work and assigning it an arbitrary relative intensity of one. The abscissa corresponding to this ordinate then had a relative intensity of 1.585. This latter reading was applied as an ordinate and the abscissa corresponding to it then had a relative intensity of $(1.585)^2$. This process was continued until a per cent transmission lower than any used in the experimental work was reached. A plot of log per cent transmission against log relative intensity gave the desired emulsion calibration curve. The calibration curve corresponding to the preliminary curve given in Figure 3 is shown in Figure 4.

C. Preliminary Experiments

It was necessary to give some attention to the form of the sample which could be used for excitation. Although Feldman (10) successfully excited solutions of zirconium, it

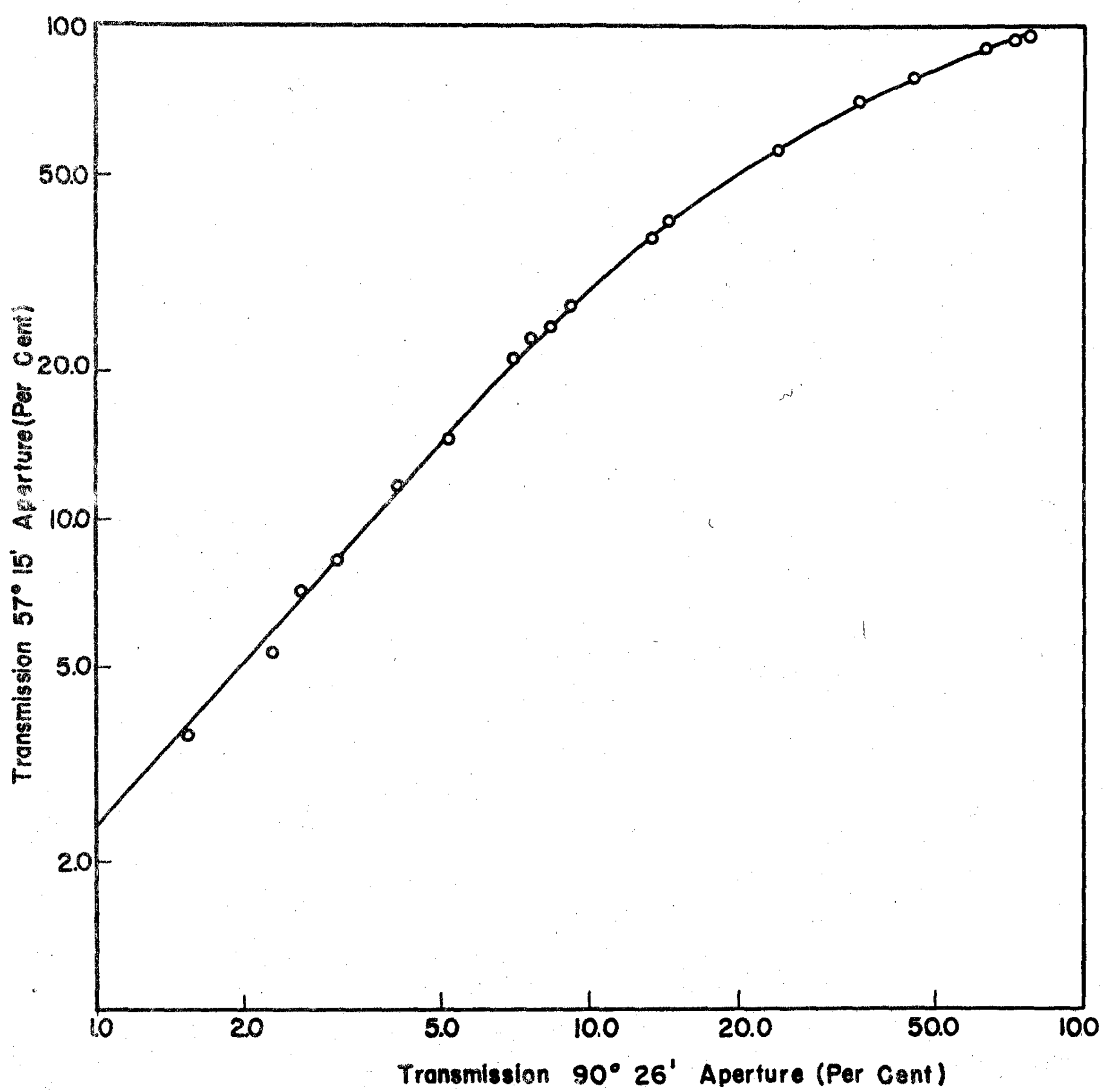

Figure 3. Preliminary Curve for Emulsion Calibration

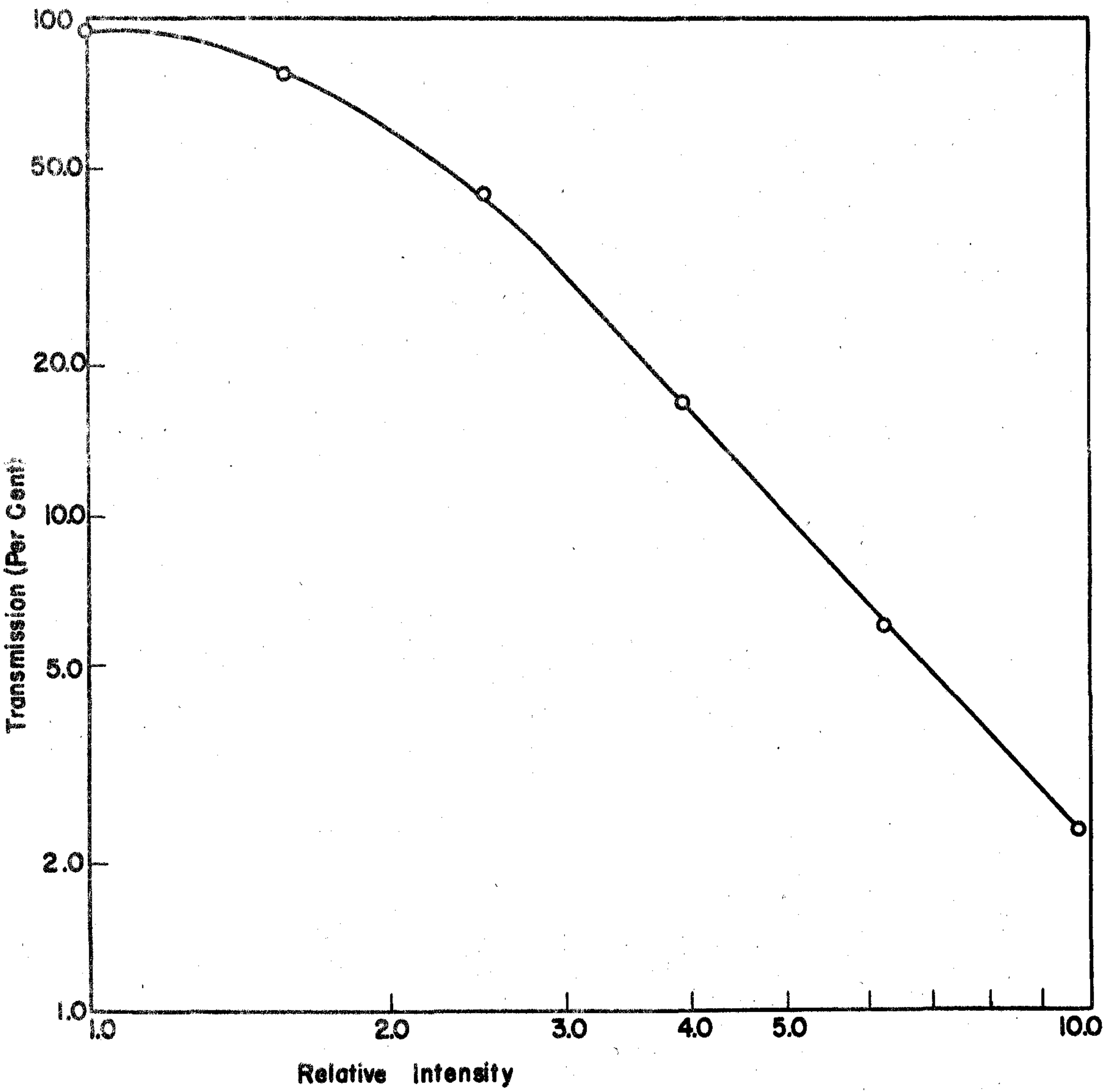

Figure 4. Emulsion Calibration Curve for Eastman
Type S. A. No. 1 Plate

was felt that any method of analysis using such solutions would be limited to soluble salts. Since it is difficult to dissolve zirconium oxide, and since this is one of the more common forms of zirconium, such a method would not be practical for analyzing oxide samples. On the other hand, since it is relatively easy to convert practically all zirconium salts (the phosphate is a notable exception) to the oxide, it was decided that this would be the logical sample form.

Some preliminary experiments were carried out using a high-amperage d.c. arc as the exciting source on a mixture of graphite and oxide. Strock and Drexler (62) and Feldman (10) had previously observed that the refractory nature of zirconium oxide caused difficulties in obtaining a reproducible vaporization and excitation in this type of discharge. This observation was confirmed in our studies, and it became evident that if a high-precision method of analyzing hafnium-zirconium mixtures were to be developed a more reproducible source of excitation would be necessary.

The use of an over-damped condenser discharge to excite the sample appeared to have several advantages over a conventional d.c. arc. It is possible not only to obtain a controlled, reproducible discharge, but to employ high current density discharges which impinge upon the sample surface and form sufficiently high temperatures to vaporize the zirconium oxide. Such a discharge has been used successfully to analyze cements and other mineral products (63). In these investigations the sample was mixed with graphite and pressed into pellets. The pellet was thus rendered a conductor and was used as the lower electrode.

A similar method of sample preparation was found applicable to analyzing mixtures of hafnium and zirconium oxides. Experiments concerning the oxide-graphite ratio were carried out simultaneously with those on the multisource constants. It was found that the strength of the pellet was determined by the graphite-oxide ratio, and that the pellet disintegrated if the discharge was too powerful. An oxide-graphite ratio of 1:1 behaved satisfactorily together with multisource constants 14 microfarads, 480 microhenries, and 65 ohms. Later experiments showed that an oxide-graphite ratio of 1:4 could also be used. Since the hafnium concentrates are relatively rare, this reduction in sample requirement was of value in calibrations at higher hafnium concentrations.

When the pellet was made the positive electrode, the discharge was somewhat erratic, but if the pellet was made the negative electrode this behavior was minimized. Furthermore, such a polarity was found to effect an increase in the intensity of the hafnium lines. This effect was desirable in that an increased sensitivity for hafnium could be obtained. In all the work reported here, such a polarity was used.

Since the properties of hafnium and zirconium are very similar, zirconium was the logical choice of an internal standard in determining hafnium. Since an ideal internal standard is one which possesses similar volatilization as well as excitation characteristics, an investigation of the relative volatility of hafnium and zirconium was made.

A moving-plate technique was employed in this study. The procedure consisted of making short consecutive exposures, 2 mm. in length on a plate which was moved up 3 mm. for each exposure. Representative hafnium and zirconium lines were identified and the intensity ratios of the lines were determined. This ratio was plotted against time and is shown in Figure 5. If any selective distillation took place in the discharge it would be quite evident from such a plot. It is clear from the figure that hafnium and zirconium were volatilized equally in the discharge.

If no fractional distillation occurred, it was evident that in all probability the same pellet could be used more than once. Since it would not be necessary to prepare separate samples, this would be a distinct advantage in any future studies on excitation, precision, and effects of other variables. In order to confirm this premise, an experiment was carried out in which one pellet was excited ten times and was compared with ten pellets, each excited but one time. The

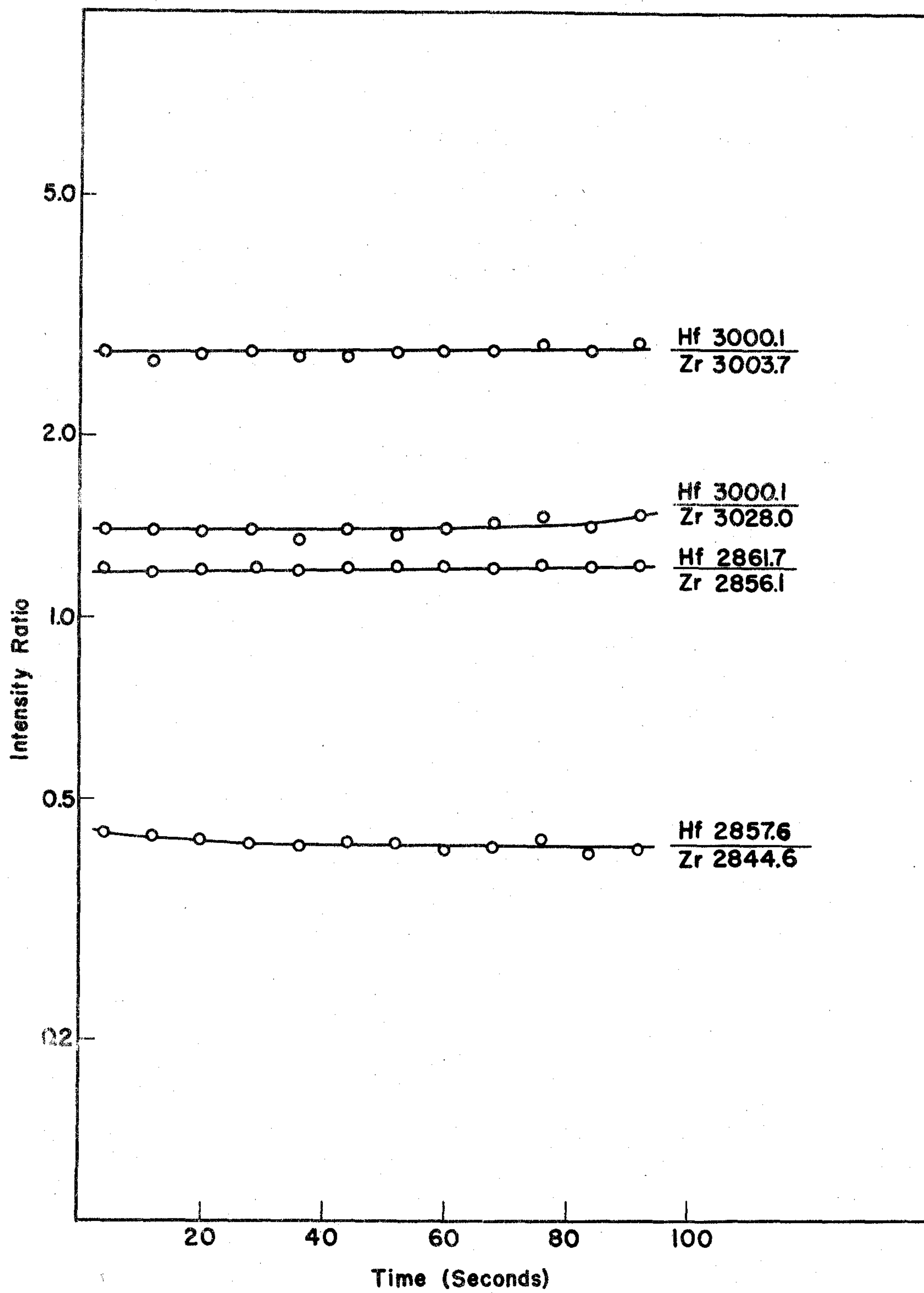

Figure 5. Variation of Intensity Ratio with Time

results are shown in Table 1. Since there was no evidence of selective excitation, it was concluded that no error was introduced when an individual pellet was excited more than once. Furthermore, in a precision study, which will be discussed later, one pellet was used for fifty determinations and showed no significant change in its intensity ratio.

Table 1.

Effect of Exciting One Pellet Ten Times Compared With Exciting Individual Pellets One Time Each

	Pellet excited consecutively		Individual Pellets
	$\frac{I_{Hf\ 2861.7}}{I_{Zr\ 2856.1}}$		$\frac{I_{Hf\ 2861.7}}{I_{Zr\ 2855.1}}$
	1.08		1.09
	1.08		1.08
	1.07		1.08
	1.09		1.07
	1.07		1.07
	1.08		1.10
	1.08		1.08
	1.08		1.10
Average	1.08	Average	1.08

The line pairs used in this research were selected with some care. The primary criterion for the choice of these lines was that the excitation potentials be similar. The reasoning which led to this restriction was discussed on page 17. It will be pointed out later that the choice of a line pair which did not possess the proper excitation characteristics resulted in a three-fold increase in the experimental error.

It was fortunate that the spark spectrum of both zirconium and hafnium had been classified (64, 65). This made it possible to choose lines which originated from the spark spectrum for the quantitative calibrations. Such lines originate in higher energy levels and should be subject to a minimum of self-reversal. Since the ionization potential of zirconium has been determined (66) as 6.93 electron volts, the excitation potential of the ZrII lines could be calculated.

There is some disagreement in the value of the ionization potential of the neutral hafnium atom. Hubbard and Meggers (67) list its value as approximately 5.5 e.v. but Finkelnburg (68) claims it should be 7.6 e.v. Finkelnburg's value was calculated from regularities in the screening increment throughout the periodic table. Meggers intimates (69) that his value is based on some unpublished data. All values of the excitation potentials for hafnium lines are arbitrarily based on Meggers' value of the ionization potential.

Line pairs were selected which would be relatively free from interferences. Since iron and titanium almost invariably are found in zirconiferous materials, particular care was taken to use lines which were not subject to serious interference from lines of these elements.

Certain photometric considerations also were factors in choosing a line pair. Since the sensitivity and response of the photographic emulsion change with wave length, it is desirable to choose line pairs within 25 A of each other. This criterion was adhered to fairly closely except in the case of HfII 3109.1 and ZrII 3164.3. Since the plate response changes very little with wave length in the region, and since the other considerations were favorable, in this case a larger wave length interval was necessary. The fact that it was advantageous to use intensity ratios near unity was an additional factor in choosing line pairs. The reasons for such a choice have been discussed previously in this paper.

The line pairs which were chosen for the quantitative calibrations are listed in Table 2. The wave lengths are those listed in the Massachusetts Institute of Technology Wave Length Tables (70).

D. Analysis of Hafnium-Zirconium Mixtures

The expression relating intensity ratio and concentration was shown previously to be

$$\log \frac{I_A}{I_B} = n \log \frac{C_A}{C_B} + k$$

Table 2.
Line Pairs Used for the Analysis of Hafnium-Zirconium Mixtures

Line pair Å	Ratio of excitation potential (electron volts)	Range (per cent hafnium)
HfII 2861.696 / ZrII 2856.065	10.3 / 11.9	0.05-6.4
HfII 2861.696 / ZrII 2839.339	10.3 / 11.8	6.4-20
HfII 2975.882 / ZrII 3003.736	10.3 / 11.6	20-44
HfII 3109.117 / ZrII 3164.310	10.3 / 11.7	31-58
HfII 3000.096 / ZrII 3003.736	10.1 / 11.6	54-78
HfII 3000.096 / ZrII 3028.040	10.3 / 11.9	72-89
HfII 2857.650 / ZrII 2844.579	11.4 / 12.3	89-99

This expression holds for the case in which mixtures of hafnium-zirconium are being analyzed, and in the working curves log intensity ratio was plotted against log (Hf/Zr x 100).

1. Quantitative calibrations

When this research was started, neither hafnium-free zirconium nor zirconium-free hafnium was available. A sample of zirconium oxide which contained about 0.3% HfO_2 was obtained from the Oak Ridge National Laboratory. Hafnium oxide which was represented as 98.5% HfO_2 was obtained from the De Rewal International Rare Chemicals Company. Qualitative analysis of both samples showed only traces of titanium, iron and silicon as impurities. A preliminary determination of the zirconium content of the hafnium oxide sample was made by adding an additional 1.5% ZrO_2 and determining the relative change in intensity in some hafnium and zirconium lines. It was found that the labeled percentage was correct within one or two per cent. (This was in contrast to a previous experience when a sample labeled 99.5% HfO_2 was actually about 40%).

Standard samples were first made up by a dry grinding technique on the basis of pure zirconium oxide and 98.5% hafnium oxide. The initial standards were prepared to contain 0.25% to 5.0% hafnium.

The standard samples were fused with potassium bisulfate and the melt was dissolved in 10% sulfuric acid. The melt was then poured into 300 ml. of distilled water water and the acid just neutralized with 10% sodium hydroxide solution. The hydrated oxides were then precipitated with ammonium hydroxide. The precipitate was washed by decantation, dissolved in the smallest amount of sulfuric acid, and reprecipitated with ammonium hydroxide. The hydroxide was filtered, washed, dried and ignited to the oxide. The ignition was carried out in a muffle furnace at 800°C. for two hours. Several control experiments were carried out in order to establish that no fractionation took place during this procedure.

All other standard samples were prepared from standard solutions of zirconium and hafnium. A 10% sulfuric acid solution was necessary to prevent hydrolysis. In all cases a double precipitation of the hydroxides was carried out. This prevented the co-precipitation and adsorption of alkali metal ions.

The initial standard samples were mixed in a 1:1 ratio with Special Spectroscopic Graphite Powder, (National Carbon Company, Grade SP-1). All other standards were mixed in a 1:4 ratio with this graphite. A total of 500 mg. sample was prepared and pressed into 1/4 in. diameter pellets with an ARL briquetting press at a total load of 8000 lbs.

The pellets were excited and photographed under the conditions listed in Table 3.

All the line pairs except one, HfII 2861.7/ZrII 2856.1, were sufficiently free from a continuous background so that no corrections for this interference were necessary. In the case of the single exception, background corrections were made by subtracting the intensity of the background from the intensity of the line plus background.

Duplicate exposures were made of each standard sample on two plates -- a total of four exposures for each standard.

Table 3.

Summary of Operating Conditions for Analyzing Hafnium-Zirconium Mixtures

Spectrograph	Jarrell-Ash 21-ft. stigmatic grating spectrograph with optical system previously described (p. 39)
Upper electrode (positive)	Graphite rod, 1/8 in. diameter and 1 in. long pointed at one end
Lower electrode (negative)	Cylindrical pellet prepared as described above
Analytical source	An overdamped 60 cycle d.c. discharge with arc-like characteristics obtained from ARL Multisource with the following constants: Capacitance: 14 microfarads Inductance: 480 microhenries Resistance: 65 ohms Phase angle: 30 degrees
Exposure time	20 seconds
Slit	0.05 mm.
Emulsion	SA No. 1 (Eastman Kodak Co.)
Wave length region	2300-3500 A
Order	First
Sector	7-step sector
Development	4 minutes at 21°C. in D-19 with continuous agitation
Densitometry	ARL Comparator-Densitometer

Since the zirconium oxide contained some residual hafnium and the hafnium oxide contained some residual zirconium, it was necessary to determine the amount of residual present in each. This was done by the method of zero intercepts (71). A plot was made on millimeter coordinate paper of intensity ratio vs. concentration (Hf/Zr x 100) of standard as prepared, i.e., the zirconium oxide was assumed pure. When the points were extrapolated to zero Hf/Zr x 100, it was found that this gave a finite value of the intensity ratio. Since such a plot must give zero intensity ratio at zero per cent hafnium, the curve was displaced laterally so that it passed through the origin. The amount of this displacement was then a measure of the hafnium content of the zirconium oxide.

A similar correction was made for the zirconium remaining in the De Rewal hafnium oxide. Later in this research a more highly purified sample (labeled 99.5% HfO_2) was obtained, and the same technique applied to determine the residual zirconium. After allowing for the zirconium content of the two samples of hafnium oxide, working curves prepared from each coincided.

Figures 6 and 7 show the magnitude of the corrections which were applied.

A sample of zirconium oxide containing negligible hafnium ($\sim$300 parts per million) also became available from

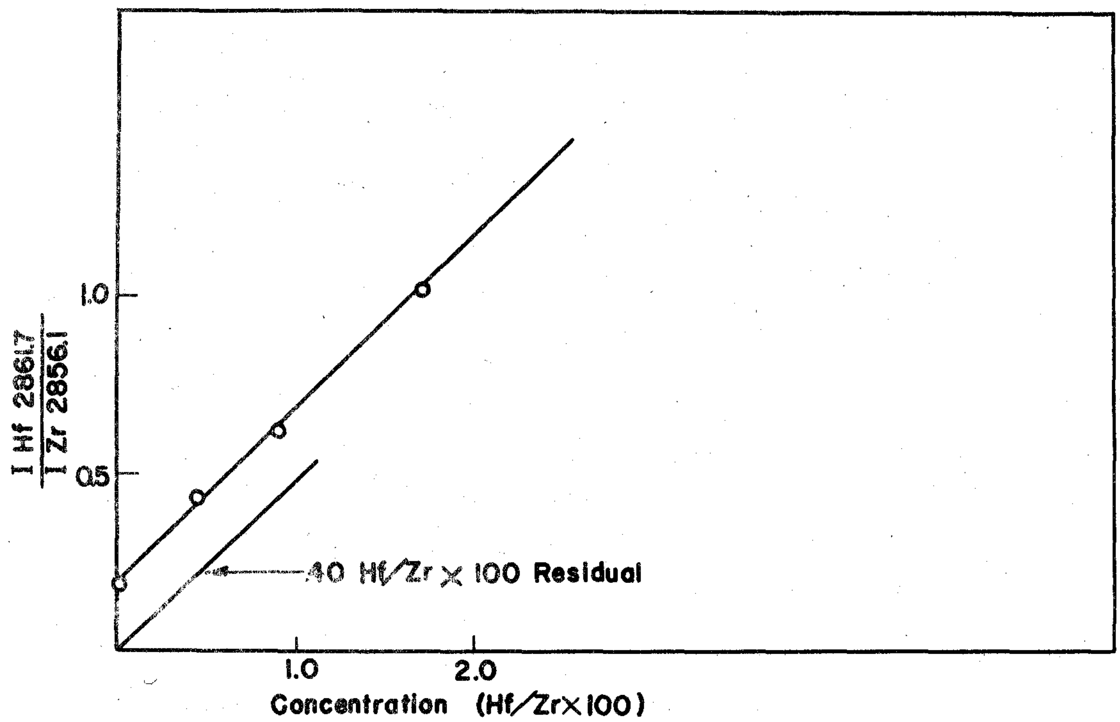

Figure 6. Correction for Residual Hafnium in Zirconium Oxide

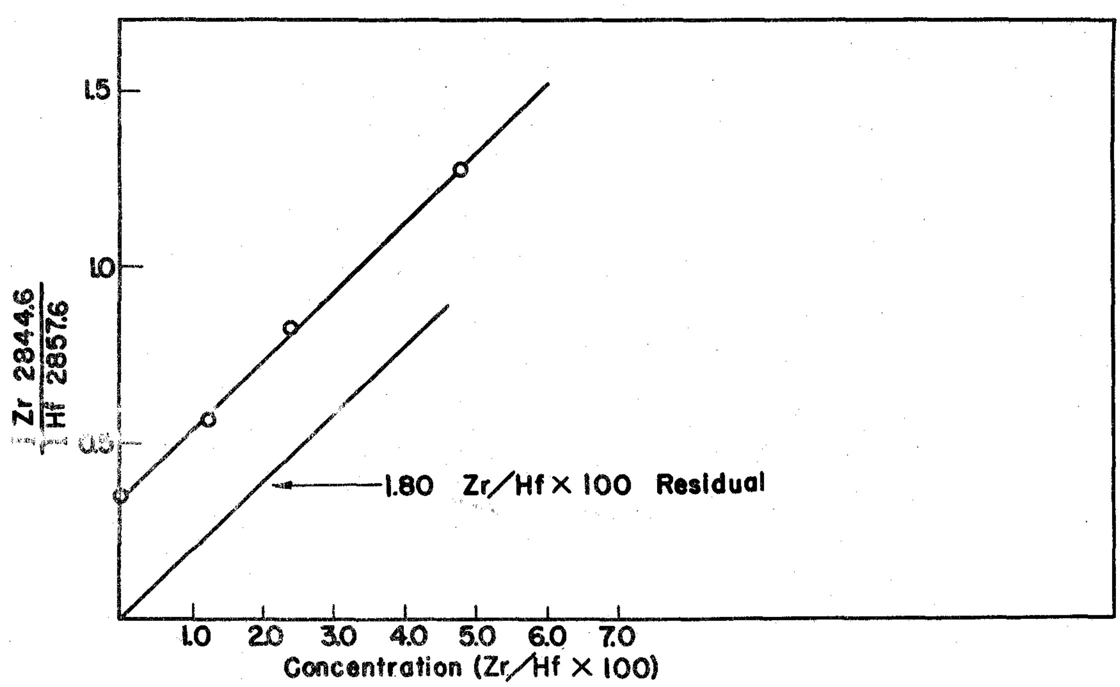

Figure 7. Correction for Residual Zirconium in Hafnium Oxide

Foote Mineral Company (Philadelphia, Pennsylvania). Standard samples for the range Hf/Zr = .04-350 then were prepared on the basis of pure ZrO_2 and HfO_2 containing 1.80 Zr/Hf x 100.

The final working curves for the mixtures were obtained by plotting log intensity ratio against log Hf/Zr x 100. They are shown in Figure 8. With one exception the working curves are all close to the theoretical slope of one. This fact serves to demonstrate that little or no self-absorption took place. The exception, the line using HfII 2861.7 and ZrII 2839.3, has a slope somewhat less than one. This was observed, it is believed, because of the presence of a small amount of continuous background for which a correction could not be made.

2. Effect of operating variables

Mixtures of hafnium and zirconium should constitute an ideal combination to study from the point of view of the internal standard principle. Line pairs having very similar as well as two-fold differences in excitation potential were available for study. Since it has been shown that there was no difference in the relative volatility of the two elements, varying the experimental conditions could be compared between such classes of line pairs.

a. Type of excitation Hasler (41) has shown that a multisource unit, by a variation of only the resistance

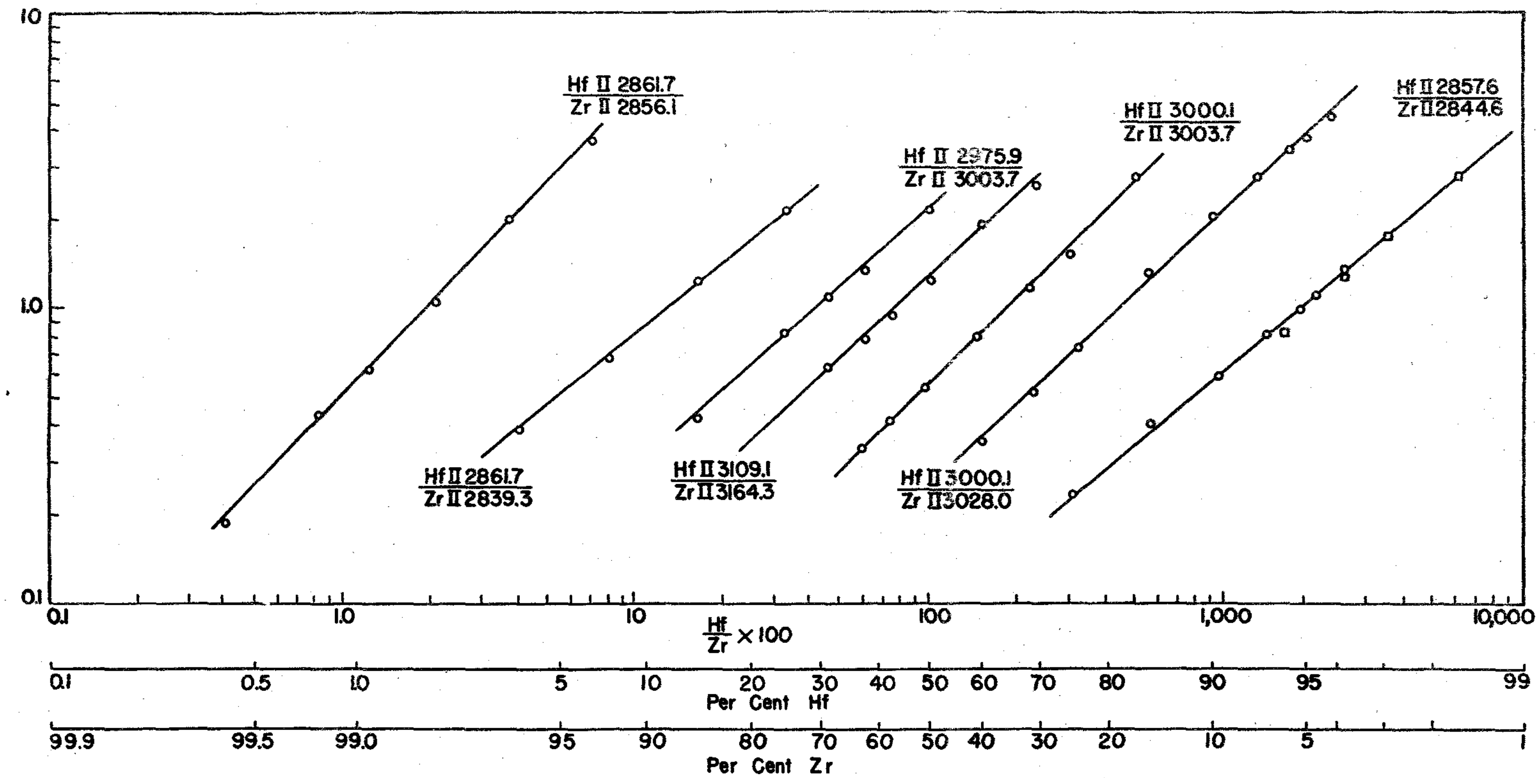

Figure 8. Working Curves for Analyzing Hafnium-Zirconium Mixtures

parameter, can give a variety of excitation conditions. He shows that, for a given inductance and capacitance, the discharge changes from an arc-like to a critically damped (spark-like), then to an overdamped discharge having arc-like characteristics when the resistance is gradually increased. Several line pairs were measured under such widely varying excitation conditions. Figure 9 shows the variations which were observed in the different line pairs. It is interesting to note that the line pairs HfII 3109.1/ZrII 3164.3 and HfII 3000.1/ZrII 3003.7 are as constant as the pairs HfII 2975.9/HfII 3109.1 and ZrII 3164.3/ZrII 3003.7. That the line pair HfII 2975.9/ZrII 3003.7 exhibits a definite increase in its ratio is difficult to explain, since its ratio of excitation is nearly the same as the previous HfII/ZrII line pairs.

Line pairs which possessed two-fold differences in excitation potential might be expected to exhibit marked changes in their intensity ratios under the conditions of the experiment. This is actually what was observed. It will be noted that not only the HfII/ZrI ratios, but also the ZrII/ZrI ratios varied quite considerably. While a more quantitative study of the precision of the two classes of line pairs will be presented later, it will be noted that the precision of line pairs having a marked difference in excitation potential is much less than that for the other line pairs.

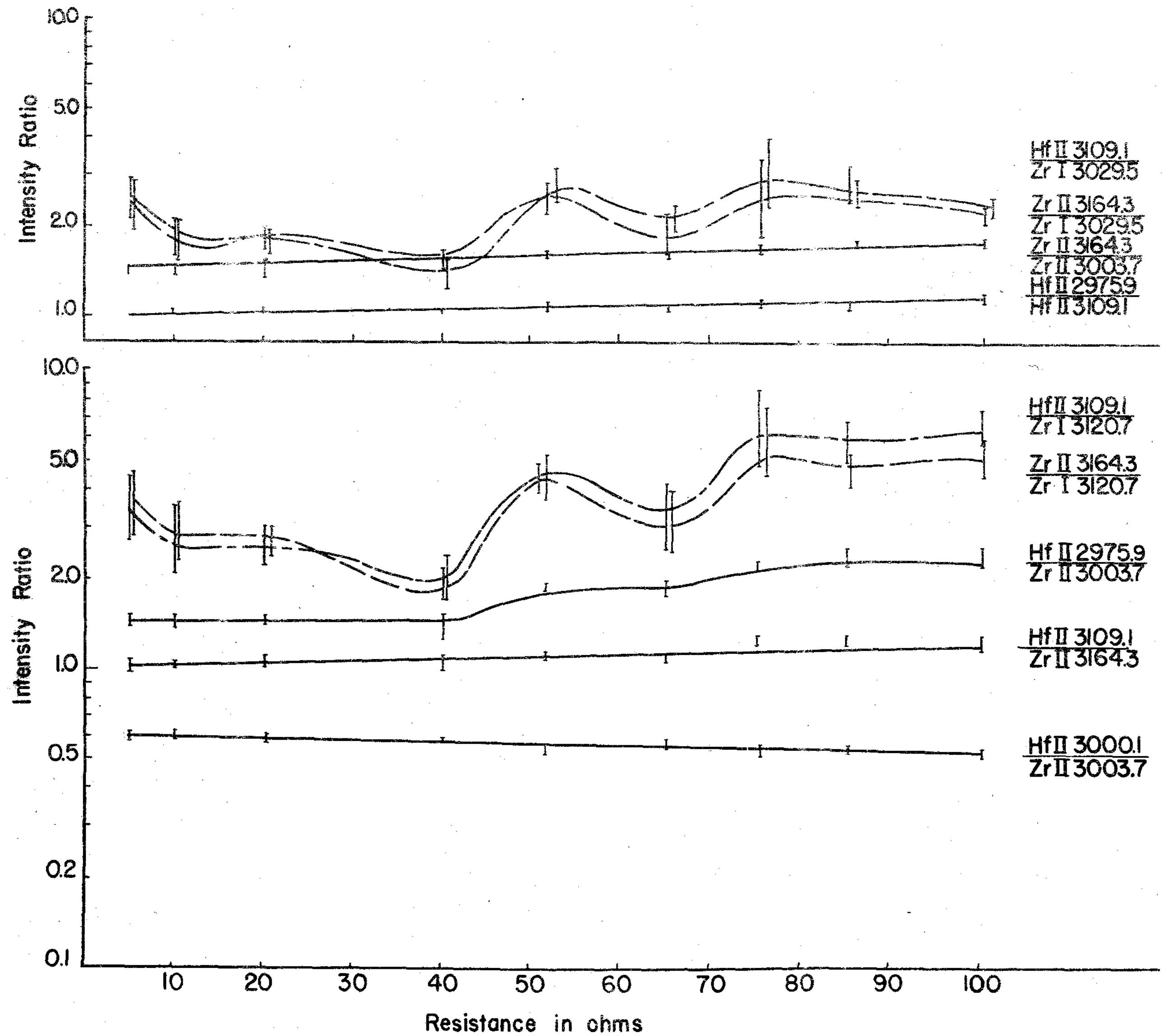

Figure 9. Variation of Intensity Ratios with Discharge Conditions

b. Extraneous materials The effect of the presence of other impurities on intensities has been discussed previously in this work (p.23). Such an effect was studied in the system under consideration with two different materials. Sodium chloride was chosen for this study because sodium possesses a low resonance potential and sodium chloride is quite volatile. The addition of this compound afforded an extreme test of the effect of extraneous materials. Calcium was also studied because it is a common impurity.

In the first case, sodium chloride in varying amounts was mechanically mixed with a sample of zirconium oxide containing 2.7% hafnium. The pellets were excited and the intensity ratio of HfII 2861.7/ZrII 2856.1 and HfII 2822.6/ ZrI 2821.6 were determined. A similar study, except for line pairs, was made using calcium as the extraneous element. In this case the calcium was added to a solution of zirconium and hafnium, the hydroxides precipitated, evaporated to a slurry, and ignited to the oxide. In this manner the calcium should form a more intimate mixture than could be obtained by dry grinding.

Figure 10 shows that in the case of the system under observation, the effect of these added materials can be neglected. It will be noted that even those line pairs which have an unfavorable relationship of their excitation potentials

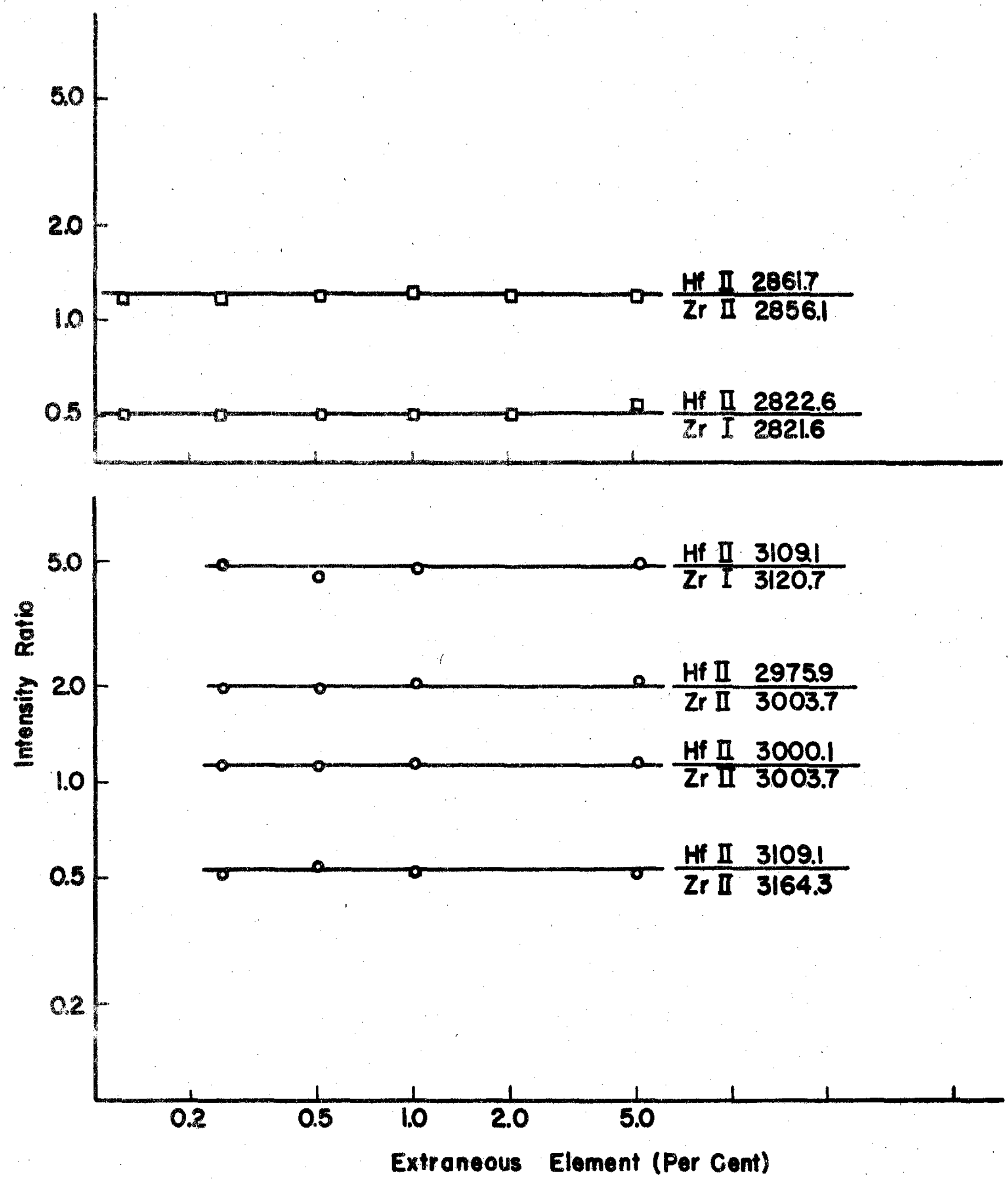

Figure 10. Effect of Extraneous Materials on Intensity Ratio

□ Sodium Chloride
o Calcium

show the same lack of response on the addition of extraneous elements as do the other line pair. This indicates that the type of discharge which was used tended to eliminate the effects of such added materials.

c. Base materials In view of the constant intensity ratios which had been observed under widely varying excitation conditions, and in the presence of extraneous elements, an experiment was carried out to show whether or not different zirconium salts could be used for analysis directly. Zirconium pyrophosphate, selenite, and zirconyl nitrate, sulfate and chloride were prepared from the same base material. Pellets of these salts mixed with graphite were prepared and excited. Table 4 shows the average of triplicate exposures. It will be noted that such salts may be used directly in carrying out an analysis.

Table 4.

Effect of Using Zirconium Salts as Base Materials

Base material	$\frac{I_{Hf\ 2975.9}}{I_{Zr\ 3003.7}}$	$\frac{I_{Hf\ 3109.1}}{I_{Zr\ 3164.3}}$
ZrO_2	1.75	1.07
$Zr(P_2O_5)_2$	1.73	.98
$ZrOCl_2$	1.72	1.04
$ZrO(NO_3)_2$	1.68	.98
$ZrOSO_4$	1.62	.99
$Zr(SeO_3)_2$	1.74	.99

A similar experiment was carried out using some zirconium metal which had been prepared at the Bureau of Mines. The metal was machined to 1/4 inch diameter rods and was excited along with zirconium oxide pellets which had been prepared from the same metal. Zirconium turnings from this metal were also pressed into pellets and excited. Because preliminary experiments showed differences in the intensity ratios, nine exposures of each sample were made to see if the observed differences were significant. Table 5 shows a comparison of the three samples in which the value reported is an average of nine determinations.

Table 5.

Comparison of Hf/Zr Intensity Ratios Using Pellets of Zirconium Oxide and Electrodes of Zirconium Metal

Sample	$\frac{I_{Hf\ 2861.7}}{I_{Zr\ 2856.1}}$
Zirconium oxide	1.22
Zirconium metal	1.16
Zirconium metal turnings	1.31

There appears to be definite evidence that there are significant differences in the intensity ratios. This is somewhat difficult to explain, although one may postulate that in the case of the oxide, there may be a slight difference in rates of decomposition. This would then be reflected in a lower intensity ratio.

d. Graphite-oxide ratio The effect of using varying graphite-oxide ratios were investigated. The results are tabulated in Table 6.

Table 6.

Effect of Graphite-Oxide Ratio on Intensity Ratio

Graphite-oxide ratio	$\frac{I_{Hf\ 2975.9}}{I_{Zr\ 3003.7}}$	$\frac{I_{Hf\ 3109.1}}{I_{Zr\ 3164.3}}$	$\frac{I_{Hf\ 2869.7}}{I_{Zr\ 2839.3}}$
2:1	.437	.229	1.16
4:1	.428	.225	1.16
6:1	.423	.222	1.16

Apparently changes of this ratio have little effect on the line pair intensity.

e. Crystal structure In their studies on the spectrographic analysis of cements, Hasler and co-workers (63) found it necessary to reduce their samples to a standard form. It had been reported (72) that it was necessary to use a standard crystalline form of zirconium in order to obtain consistent results. In view of the work described previously it was thought that the internal standard principle would correct for such variations in crystalline form. A sample of zirconium-hafnium hydroxide was ignited under three different conditions, one at 125°, a second at 700° and a third at 1100°. All were ignited for two hours. The latter two samples should possess different crystalline forms. The results are summarized in Table 7.

Table 7.

Effect of Temperature of Ignition on Intensity Ratio

Temperature °C.	$\frac{I_{Hf\ 2861.7}}{I_{Zr\ 2839.3}}$	$\frac{I_{Hf\ 2975.9}}{I_{Zr\ 3003.7}}$	$\frac{I_{Hf\ 3109.1}}{I_{Zr\ 3164.3}}$
125	1.18	.413	.227
700	1.20	.414	.226
1100	1.16	.409	.226

The conclusion which may be drawn is that there is little or no variation of intensity ratio with changes in crystal structure in this system.

3. Precision

Much of the data concerning the precision of spectrochemical methods which are in the literature were obtained by making a number of exposures on a single photographic plate. Such a procedure gives a false precision because errors which arise from the photographic photometry are less than would ordinarily be encountered. All precision studies which are reported in this work were obtained from single exposures on separate photographic plates. In order to minimize errors which might be attributed to the emulsion grain, transmittancy readings were made on two or more steps, i.e. all those steps in which the transmittancies of the spectral lines were between 7% and 75%.

The intensity ratio Hf 2861.7/Zr 2856.1 of one standard sample was determined 50 times on 50 separate plates. A routine spectrographer excited this sample and determined its intensity ratio together with routine samples with no extraordinary precautions. This precision was a measure of what might be expected for routine determinations. The per cent standard deviation for single determinations on this sample was 1.40. Four values were discarded in this calculation because their deviations were more than three times the standard deviation. A histogram of the distribution of intensity ratios is shown in Figure 11.

The precision of other line pairs was determined by exposing samples of appropriate concentrations twelve times on twelve different plates. In order to illustrate the importance of choosing the proper lines, the precision of intensity ratio of two lines having an unfavorable ratio of excitation potential was determined. The precision data are tabulated in Table 8. It is significant to note that the precision of the line pairs having similar excitation potentials (which were used in the preparation of the working curves) have a per cent standard deviation in the order of

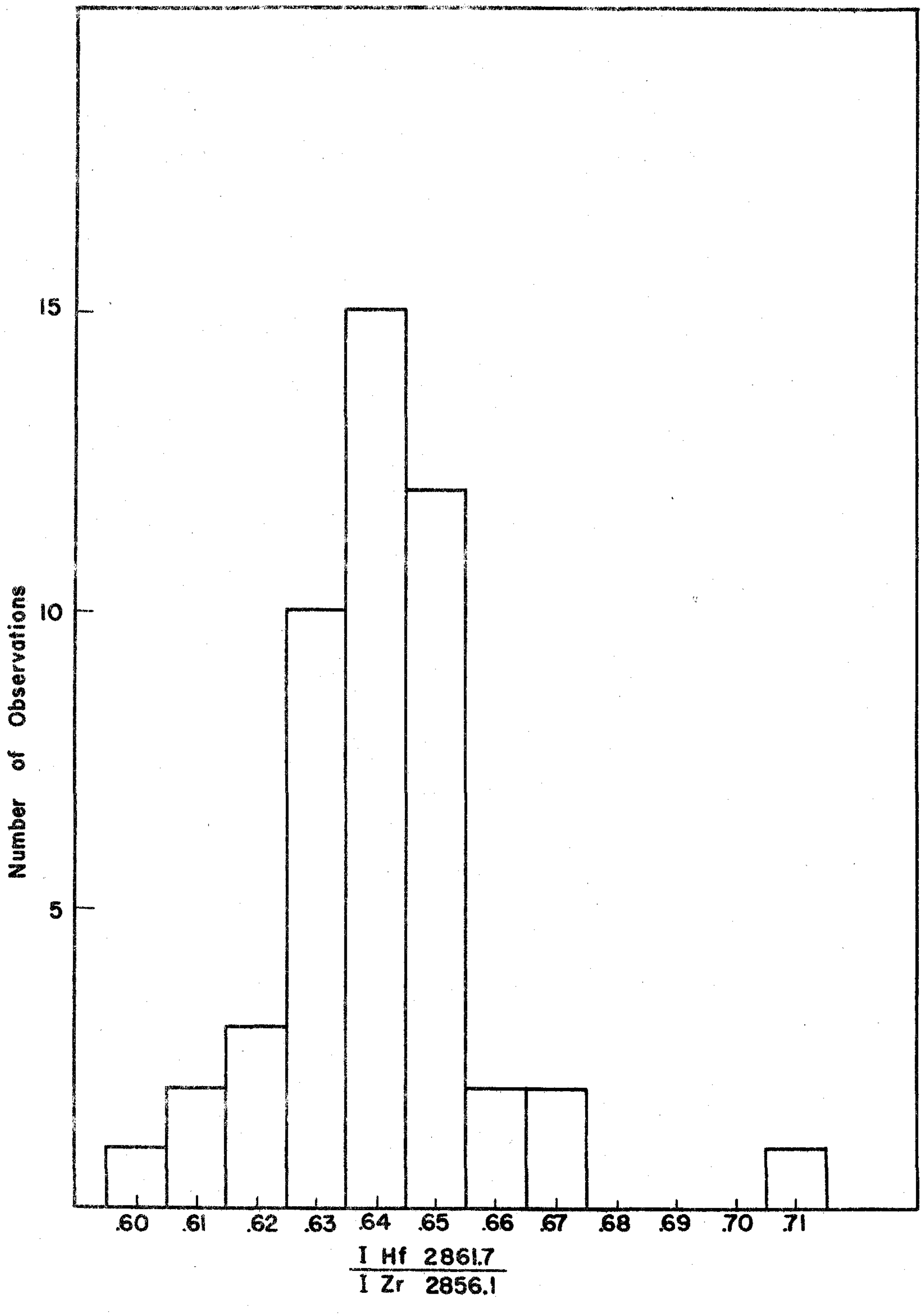

Figure 11. Distribution of Intensity Ratio for Sample ZK-301

1-2% while that of unfavorable line pair HfII 2975.9/ZrI 3022.5 is 5.05%.

Table 8.

Precision Study of Line Pairs

Sample No.	Per cent hafnium	Line pair	Per cent standard deviation
1	13.8	HfII 2861.7 / ZrII 2839.3	1.26
2	37.5	HfII 2975.9 / ZrII 3003.7	1.68
2	37.5	HfII 2975.9 / ZrI 3029.5	5.05
3	50.0	HfII 3109.1 / ZrII 3164.3	1.96
4	69.2	HfII 3000.1 / ZrII 3003.7	1.35
5	85.1	HfII 3000.1 / ZrII 3028.0	1.95
6	95.4	HfII 2857.6 / ZrII 2844.6	.87

4. Accuracy

A measure of the accuracy of this method was obtained in three ways: (a) comparison with standard samples prepared by an independent laboratory, (b) comparison with independent spectrographic results, and (c) comparison with a chemical method.

Standard samples which were prepared at the New Brunswick Laboratory of the Atomic Energy Commission by the addition of known amounts of hafnium oxide to hafnium-free zirconium were analyzed by an independent observer. The results are shown in Table 9.

Table 9.

Comparison of Spectrographic Results with New Brunswick Laboratory Standard Samples

Sample	Per cent hafnium As prepared	Per cent hafnium Spectrographic
A	2.00	2.04
B	1.00	1.00
C	0.50	0.50
D	0.20	0.21
E	0.10	0.09
F	0.05	0.042
X	0.00	not detected

Since values below Hf/Zr x 100 = .30 were obtained by extrapolating the working curve, it might be expected that the accuracy was better above this point. Other values are in excellent agreement with the New Brunswick standards.

Table 10 also shows a comparison with spectrographic results which were obtained at the Oak Ridge National Laboratory and at the National Bureau of Standards.

Although chemical methods are usually used as a measure of the accuracy of a spectrographic method, in this case under

Table 10.

Comparison of Spectrographic Results

Sample	Per cent hafnium in mixed oxides: Pellet method	Oak Ridge	National Bureau of Standards
1	.30	.23	.30
2	.86	.85	--
3	2.96	3.11	--

consideration it is somewhat doubtful if such a criterion applies. The selenite method, described previously, is not a simple procedure and suffers from errors which were previously discussed. Nevertheless, spectrographic determinations of the hafnium content were made on some mixed oxide samples which had been analyzed by the selenite method by Prof. E. M. Larsen of the University of Wisconsin (73). A comparison of results are tabulated in Table 11.

Table 11.

Comparison of Spectrographic and Chemical Determinations

Sample	Per cent hafnium in mixed oxides: Spectrographic	Chemical
A	9.54	9.18 ±0.3
B	13.3	14.72 ±0.3
E	35.0	36.93 ±0.2
H	50.0	50.56 ±0.2
I	63.0	64.79 ±0.2
J	71.9	72.52 ±0.3

It will be noted that, with the exception of sample A, the values obtained by Prof. Larsen are consistently high compared with our results. He states that the oxides were pure binary mixtures, but that the selenium dioxide which he used to prepare the selenious acid was contaminated by some unknown element. The contaminant imparted a slightly brown color to the ignited oxides.

It is possible that the spectrographic determinations would check better with the selenite if this contaminant were not present. At the time of this thesis no other results were available from Prof. Larsen.

V. SUMMARY AND CONCLUSIONS

It has been demonstrated that the hafnium content of mixtures containing zirconium and hafnium may be determined spectrographically over the range 0.1-99 per cent. The accuracy of the method compared very well with independently prepared standard samples and independent spectrographic methods. Comparison with chemical analyses were satisfactory, but tentatively were somewhat low. The precision for single determinations averaged 1.50 per cent standard deviation. A line pair whose excitation potentials differed by a factor of two was shown to have a per cent standard deviation of 5.05.

Studies were made on the effect of changing the experimental variables, e.g., the discharge conditions, the base materials, the oxide-graphite ratio, the crystal structure of the oxide and the presence of extraneous materials. It was found that these variables, with the exception of using metallic materials as samples, had little or no effect on the ratios of line pairs whose excitation potentials were similar. The ratios of lines whose excitation potentials differed by a factor of about two showed a wide variation under changing discharge conditions. However, such line pairs were not affected by the addition of extraneous materials.

This method of analysis should prove a useful tool for the further understanding of the chemical properties of these elements.

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