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UNITED STATES  
DEPARTMENT OF THE INTERIOR  
J. A. Krug, Secretary

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BUREAU OF MINES  
R. R. Sayers, Director

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REPORT OF INVESTIGATIONS

A METHOD FOR THE SPECTROCHEMICAL DETERMINATION  
OF GERMANIUM, TIN, AND LEAD IN ORE SAMPLES



BY

GRAHAM W. MARKS AND H. TRACY HALL

REPORT OF INVESTIGATIONSUNITED STATES DEPARTMENT OF THE INTERIOR—BUREAU OF MINESA METHOD FOR THE SPECTROCHEMICAL DETERMINATION OF  
GERMANIUM, TIN AND LEAD IN ORE SAMPLES<sup>1</sup>By Graham W. Marks<sup>2</sup> and H. Tracy Hall<sup>3</sup>CONTENTS

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## INTRODUCTION

Accurate methods for the quantitative spectrochemical determination of the constituents of ore samples would be of great value in the chemical and metallurgical industries, as spectrographic methods of analysis are, in general, much more rapid than chemical methods. The spectrograph permits determining simultaneously the concentrations of several elements. Even a qualitative spectrographic analysis of an ore prior to making quantitative chemical analyses obviates much unnecessary work. Semiquantitative analyses often are useful for determining whether or not certain elements are present in sufficient concentration to make their extraction worthwhile. The ideal procedure should be directly applicable without preliminary chemical separations and should yield results as accurate as those obtained from the best chemical procedures. Much spectrographic work on minerals and ores has been done as is shown by an examination of the bibliography of Meggers and Scribner<sup>4</sup> and by a review of the Abstract literature. However, methods of analysis are only qualitative or, if quantitative, only applicable to particular minerals, ores, concentrates, or chemical separations therefrom, and usually are designed to determine one or a very few elements.

The internal standard method does not seem suitable for the general analysis of ores. Some workers have used the internal standard method by adding an extraneous element in known amount to the sample. This procedure probably is satisfactory if the composition of the ores or minerals under investigation does not differ too greatly. Standard curves prepared under such conditions would not be generally applicable. It is not to be expected, for example, that an internal standard prepared for the determination of lead in a particular type of zinc ore would be accurately applicable to the determination of lead in a copper ore.

We believe that the so-called total-energy method of Slavin,<sup>5</sup> which makes use of the direct-current arc, can be applied generally and will yield reasonably accurate and consistent results. This method does not eliminate the possibility of one element affecting the line intensities of another volatilized simultaneously in the arc. We know no prior investigations on the influence of extraneous elements on line intensities that employ this method.

Basically, the preparation of proper standards for analysis of the minor constituents of ores must rest upon knowledge of the effects of the major constituents upon the line intensities of the former. Once knowing these effects, it should be possible to remedy them somewhat. As the spectra of the elements in any subgroup of the periodic table are similar,<sup>6</sup> and vapor pressures and boiling points of such elements, as well as like compounds, roughly correspond, the influence of the matrix upon line intensities would be expected to be much the same using the same methods of excitation, particularly for spectra belonging to the same series. Therefore, in these studies several elements in one group were studied simultaneously. The major constituents of the ores containing these elements were known, and the effect of the constituents upon the intensity of the spectral lines of the several elements was determined.

This paper is concerned with the determination of germanium, tin, and lead. Their distribution in ores and minerals has been discussed generally by Mellor<sup>7</sup> and others. The gangue of many ores consists largely of complex silicates. These silicates generally contain  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  in various combinations:  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{MgCO}_3$ , and  $\text{CaCO}_3$  as such are often present. Feldspars and clays, which are sometimes present, contain sodium and potassium. These investigations were concerned, therefore, with the influence of the above-mentioned oxides and their mixtures upon the intensities of certain ultra-violet germanium, tin, and lead lines with particular reference to the effect of those oxides which compose silicates.

## ACKNOWLEDGMENT

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<sup>4</sup> Meggers, W. F., and Scribner, B. F., Index to the Literature on Spectrochemical Analysis, 1920-1939: Am. Soc. For Testing Materials, 2d. ed., Philadelphia, PA.

<sup>5</sup> Slavin, M., Quantitative Analysis Based on Spectral Energy: Jour. Ind. and Eng. Chem., anal. Ed., vol. 40, 1938, p. 407.

<sup>6</sup> White, H. E., Introduction to Atomic Spectra: McGraw-Hill Book Co., New York, 1934.

<sup>7</sup> Mellor, J. W., A Comprehensive Treatise of Inorganic and Theoretical Chemistry: Vol. 7, Concerning Germanium ref. Hopkins, B. A. Chapter in the Chemistry of the Less Familiar Elements: Stipes Publishing Co., Champaign, Ill., 1939.

This paper is one of many reporting on various aspects of the Bureau of Mines' program directed toward the more effective utilization of our mineral resources.

These investigations are carried out by the Mining Branch, L. B. Moon, chief, and the Metallurgical Branch, R. G. Knickerbocker, chief. Both branches are under the supervision of R. S. Dean, assistant director.

The scope of this paper falls in the province of the Metallurgical Branch and is primarily concerned with the establishment of spectrochemical methods for the analysis of all types of ore samples whereby accurate determinations of minor and major constituents can be made with the minimum amount of work and sample preparation. This work is important in connection with the other activities of this Branch, which include the beneficiation of ores, the production of pure metals from domestic ores, the exploitation of marginal ore reserves, the recovery of secondary metals, the improvement of present industrial metallurgical practices.

With respect to this report, acknowledgment is made to S. R. Zimmerly, chief, Salt Lake City Division, Metallurgical Branch, for his active interest in this problem; H. W. St. Clair and E. V. Potter for many helpful suggestions about this work; H. C. Lukens and George North for valuable assistance in designing and constructing the arc stand; H. E. Peterson, supervisor of the Analytical Laboratory, for making the chemical analyses and providing many ore samples, and Howard Tribe and Frank Cossey, who made the photographs and drawings used in this paper.

### TOTAL ENERGY METHOD

#### Theory

The theory of the total-energy method assumes that if a sample of any material is completely volatilized in the arc, the total spectral energy obtained from any given element is directly proportional to the mass of the element present in the sample. Assuming such a linear relationship

$$m = K \int_0^t I dt$$

Or in terms of percentage,

$$Pr = 100m/M = 100K/M \int_0^t I dt$$

Where  $\underline{m}$  is the total mass of an element volatilized,  $\underline{M}$  is the weight of the sample,  $\underline{K}$  is a proportionality constant, and  $\underline{I}$  is the intensity of the radiation for a given wave length at any time,  $t$ , during the volatilization period. The total quanta of energy emitted for a stated change in atomic state of an element is directly proportional to the number of atoms of that element passing through the arc. This does not necessarily mean that every atom of the element being measured emits a specified wave length on passing through the arc, or that each atom emits this quantum of energy the same number of times. This is only true statistically if conditions in the arc remain constant.

The integration of energy emitted is performed by the photographic plate; the relative energy is determined by measuring the degree of blackening of the plate with a densitometer. The constant  $\underline{K}$  depends on the experimental apparatus, the characteristics of the photographic plate used, and the base material or diluent of the sample. When standards have been prepared,  $\underline{m}$  is known and  $\underline{K}$  can be determined. After  $\underline{K}$  has been determined,  $\underline{m}$  can be estimated in unknown samples.

The intensity,  $\underline{I}$ , of a spectral line emitted by a hot gas is given by the relationship<sup>8</sup>

$$I \sim Np e^{-h\nu/kT}$$

In which  $\underline{N}$  is the number of atoms of an element per unit volume of the gas,  $\underline{p}$  is the transition probability,  $\underline{h\nu}$  is the energy difference between the initial and final levels,  $\underline{k}$  the Boltzmann constant, and  $\underline{T}$ , the absolute temperature.

<sup>8</sup> Sawyer, A. A., and Vincent, H. B., Characteristics of Spectroscopic Light Sources: Sixth Summer Conference of Spectroscopy and its Applications: John Wiley & Sons, Inc., New York, 1939, p. 54.

Consider a sample made up of two constituents and burned in the d.c. arc under controlled conditions, that is, constant electrode separation and constant current. Assume the fused material forms a two-component system and that equilibrium exists between the molten material and the boundary layer of gas. The number of atoms of each element passing into the arc at any instant depends on the vapor pressure of the mass. If we assume Raoult's law holds at any instant, then at any given temperature

$$P_a = P_{oa} n_a \quad P_b = P_{ob} n_b$$

Where  $P_{oa}$  and  $P_{ob}$  are the pressures of the pure components  $\underline{a}$  and  $\underline{b}$ ,  $P_a$  and  $P_b$  are the partial pressures of these components, and  $n_a$  and  $n_b$  are the mol fractions of each in the molten mass.  $n_a$  and  $n_b$  change with time, as fractional distillation is occurring, and so the number of atoms per unit volume of either element in the gas becomes a function of the time,  $t$ . How  $n_a$  or  $n_b$  change during the volatilization period depends, in part, on the vapor pressure of one component with respect to the other; if one is relatively high, it is more rapidly volatilized than the other.

From the perfect gas law

$$P_a = n_a RT$$

Where  $n_a$  = number of mols of gas of component  $\underline{a}$  per unit volume

$$n_a = N_a/N_0$$

$N_0$  is Avogadro's number.

Thus

$$N_a = P_a N_0 / RT$$

If  $N_A$  and  $N_B$  are the number of molecules of  $\underline{a}$  and  $\underline{b}$ , respectively, per unit volumes of the fused mass, then

$$n_a = N_A / (N_A + N_B)$$

So that

$$\begin{aligned} N_a &= \{P_{oa} N_0 [N_A / (N_A + N_B)]\} / RT \\ &= K_0 / T (N_A) / (N_A + N_B) \end{aligned}$$

This expression shows the dependence of the number of atoms in a unit volume of the gaseous phase at any instant on the relative number of atoms of each constituent in the liquid phase at temperature  $T$ .  $N_A$  and  $N_B$  change with time, and therefore  $N_a$  changes with time. This represents conditions in the neighborhood of the boundary between the liquid and vapor phases and gives the maximum concentration in the gaseous phase. The rate of volatilization depends on the temperature, which, in part, determines the rate of movement from the boundary region. The rate of movement from the boundary region is also determined, partly by the degree of ionization and the field strength in the arc. The rapid sweep of material upward and the broadening of the arc from the base indicate that the concentration outside the boundary region is less than the maximum.

The temperature,  $T$ , is different in various regions of the arc. It depends on the energy input, the specific heats of the materials in the gaseous phase, the thermal conductivity of these gases, and the loss of energy by radiation. Even if both voltage and current could be maintained constant during the volatilization of a heterogeneous sample, the temperature of a given position in the arc would change because of the above factors, which are influenced by concentration changes. Because of this concentration change, the temperature,  $T$ , for any given position in a fixed arc is a function of the time. The presence in the arc of an extraneous element can lower the temperature and reduce the number of excited atoms of the minor constituent.<sup>9</sup>

<sup>9</sup> Elenbaas: Physics 2, 1935, p. 45.

For any particular biconstituent sample that is burned under constant conditions, that is, constant current, voltage, and electrode separation,  $\underline{T}$  can be represented as a function of the coordinates  $\underline{x}$ ,  $\underline{y}$ ,  $\underline{z}$  in the fixed arc and the time,  $\underline{t}$ .

$$T \sim f_1(x, y, z, t)$$

Likewise

$$N_a \sim f_2(x, y, z, t)$$

Thus, the total energy radiated by an element during the volatilization period and corresponding to a particular electron transition is of the form

$$E \sim \iiint f_2(x, y, z, t) P e^{-hv/(K f_1(x, y, z, t))} dx dy dz dt$$

The integrals being taken over the complete volume of the fixed arc during the volatilization period.

At the present stage of theoretical knowledge it is not possible to deduce the functions occurring in the last equation. No predictions can be made concerning the effects of extraneous elements on line intensities. Much depends on the concentrations in the arc of all the elements concerned. However, by experimentation, a great deal can be learned from which general conclusions may be drawn. In such work, conditions such as electrode separation, arc current, voltage, or power can be maintained constant by readily available means, so that their effect upon line intensities is minimized, and the effect of variations in sample composition upon line intensities can be determined with maximum accuracy. It is planned to make a series of such studies so that procedures for analyzing ores can be established and information obtained that may be of theoretical value in determining the laws of behavior of elements in mixtures burned in the arc.

#### APPARATUS

The spectrograph<sup>10</sup> used in this work has an Eagle-type mounting and has a concave grating 4 inches wide, having 15,000 lines per inch. The grating was ruled on aluminum deposited on glass, and concentrates about 80 percent of the incident light in the first order; it gives a speed of approximately  $f/30$ . The dispersion, which is approximately linear, is about  $5.6 \text{ \AA}$  per millimeter in the ultraviolet region of the spectrum. Auxiliary optical equipment consists of a plano-convex silica-glass lens having a focal length of 8 inches and a diameter of  $1\frac{1}{2}$  inches, interchangeable slits of various widths, a rotating sector, and motor and a suitable cassette and holder for photographic plates.

An electrode holder patterned after that described by Scribner and Corliss<sup>11</sup> was constructed with certain modifications and is shown in figure 1. The base plate, and base slide, the lower gear housing, and the top plate are one-piece castings made of cast iron and machined to specifications. The electrode support slides are bronze castings. Vertical movement at both top and bases is attained by means of mitre gears. The horizontal gears rest upon ball bearings. The electrode jaws were drilled to accommodate  $1/16$ ,  $1/8$ ,  $3/16$ , and  $1/2$  inch electrodes, so that any of these sizes might be aligned opposite each other, adjustment being obtained by means of a slot and clamp arrangement on the upper electrode holder.

This stand has the following advantages: (1) Convenient arrangement of parts, so that errors resulting from poor alignment can be eliminated, (2) water-cooling of the electrode clamps so that currents as high as 15 amperes can be used for an indefinite period, (3) adaptability to a variety of electrode sizes, and (4) sufficient flexibility so that other instruments, special electrodes, etc., can be mounted in and about the stand. The overall height of the holder is somewhat greater than usual.

The water-cooling system, mounted on an insulated platform, consists of a small centrifugal pump, reservoir bottle containing distilled water, and connecting tubing.

#### PLATE CALIBRATION

<sup>10</sup> Baird, W. S., A Practical Grating Spectrograph for Industrial Use: Proceedings, Sixth Summer Conference on Spectroscopy and Its Application: John Wiley & Sons, Inc., New York, 1939, p. 80.

<sup>11</sup> Scribner, B. F., and Corliss, C. H.: Jour. National Bureau of Standards, vol. 30, 1943, p. 41.

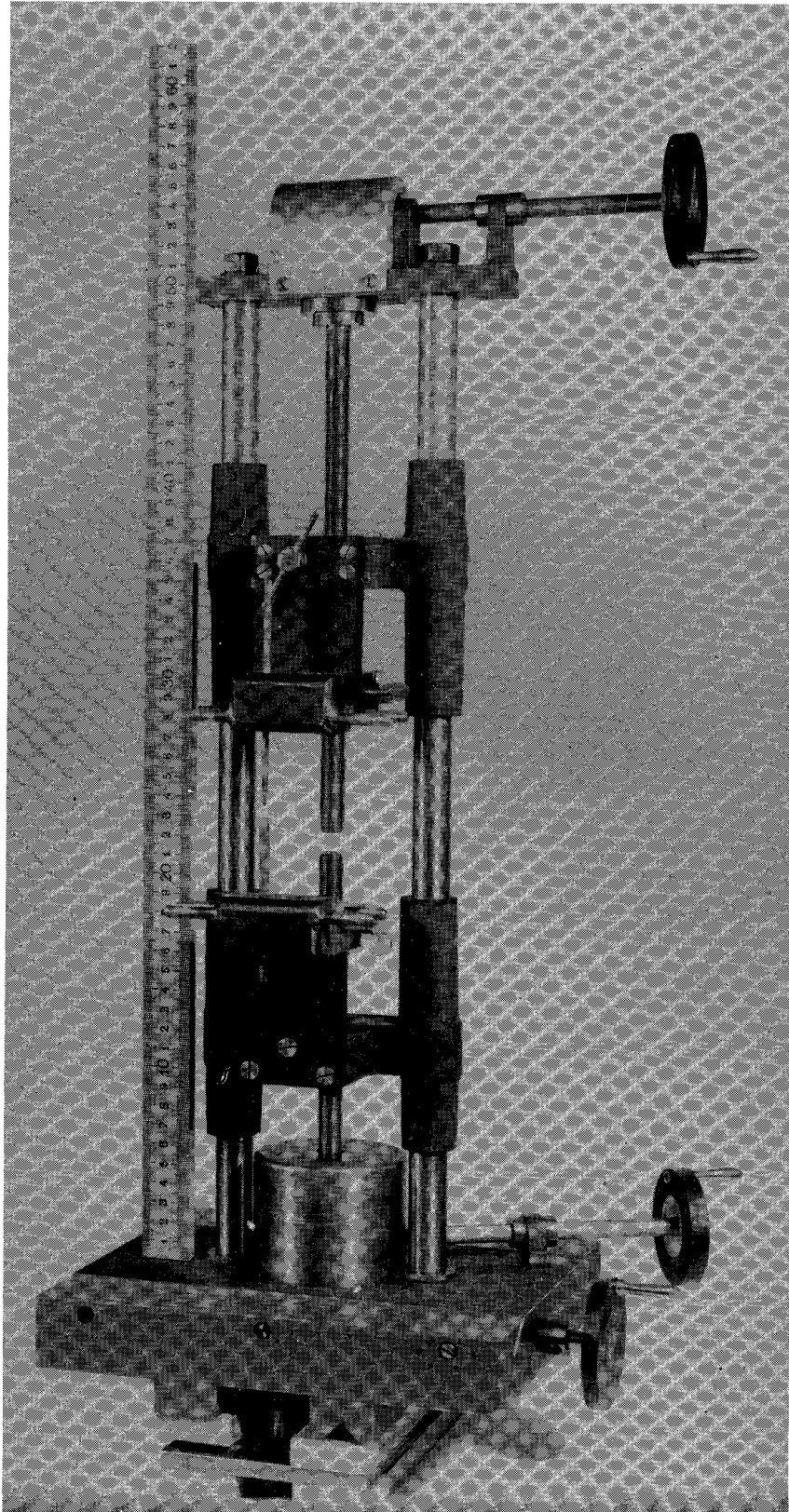


Figure 1. - Electrode holder.



In order to compare the spectrograms on one spectrographic plate with those on another, the plates were calibrated, using a standard light source. As suggested by Slavin,<sup>12</sup> the Pfund iron arc is used as a light source. An iron bead is placed in a shallow pit in a 1/2 inch lower carbon anode, and a pointed 1/8 inch-diameter carbon is used for the cathode. To use this source as a standard, it is necessary to control the current, use pure iron, fix the optical arrangements, and fix the exposure time. Only by so doing can corrections be made for the difference in emulsions when standards are being prepared or when samples are being analyzed by means of standards.

The variation of optical density with arc current for the line Fe  $\Lambda$  3091.578 Å is shown in figure 2. The slope of this line is 0.50 density units per ampere. To keep the density variation from this source less than  $\pm 0.02$  density unit requires that the current be maintained constant to within  $\pm 0.05$  ampere.

The bead should be prepared from fairly pure iron and should be approximately the same weight for each exposure. Beads prepared from Armco iron have been found to give five satisfactory and constant results if the weight of the cold, oxidized bead is between 0.25 and 0.30 gram.

Obviously, all optical arrangements, once determined, should be maintained; this includes the relative positions of the arc-stand, lens, and slit and the arc image position with respect to the grating-type spectrographs. That the latter factor is important, is shown by figure 3. The optical density decreases by 0.33 unit per inch of distance of the images from the opening in the grating mask. Limiting the permissible change in density to  $\pm 0.002$  density unit, the distance of the images should be kept constant to within  $\pm 0.05$  inch. The position of the arc was regulated so as to maintain the images of the bead and carbon electrode each 1 inch from the respective edges of the 1 inch slot in the grating mask. This can be done by mounting a double convex lens back of the arc stand and throwing an image of the arc, bead, and carbon electrode upon a ground-glass screen fixed on the wall of the laboratory. On this screen, two horizontal lines are drawn, the bottom of the bead image being kept tangent to one and the top of the carbon electrode image to the other. A line normal to the two horizontal lines is also drawn, so that the operator can keep the arc on the optical axis of the spectrograph. These lines, of course, are so placed that the images of the bead and carbon are in the desired positions with respect to the grating.

The exposure time must be the same for different tests. If the spectrograph has an a.c. electric shutter, an electric clock can be started the instant the shutter is opened. The shutter is closed electrically and the clock is stopped at the end of the time period. By this means, the interval can be timed to within  $\pm 0.05$  second.

Unless the lens is in the stigmatic position when the image is focused on the grating, a variation in line density along the length of a spectral line results. It is not always possible to use the stigmatic position with respect to the grating, but this adjustment is maintained as closely as possible.

Our method of plate calibration has been somewhat out of the ordinary. Rather than choosing a single iron line and basing the calibration on it alone, the relative intensities of the series of lines are determined and used in subsequent calibrations. The following procedure was employed: Using a rotating step sector, several spectrograms were taken on plates having the same emulsion numbers. The exposure time was 2 minutes. Several iron lines of different intensities lying in the ultra-violet region 2,500 to 3,400 Å were chosen. The gamma of the plates used does not vary greatly in this region.<sup>13</sup> The densities of the steps for each of these lines was measured, and mean values for the several spectrograms were plotted versus the logarithm of the relative transmission T of the sector opening. The transmission of the maximum opening was taken to be 100. Thus, a series of curves of optical density versus  $\log_{10} T$  were obtained. One of these curves was chosen as a reference. Values of  $\log_{10} T$  corresponding to a fixed optical density D, were read from each curve. It does not matter what value of D is taken so long as the linear portions of the curves are intersected, the curves being more or less parallel. Each of these values is subtracted from the corresponding  $\log_{10} T$  of the reference curve, and thus values of  $-\log T/T_0$  are obtained. Values of D corresponding to a 45° total sector opening are read from each curve. These data are then plotted against  $2-\log T/T_0$ , the 2 having been introduced to reverse the curve. Hereafter the expression,  $2-\log T/T_0$  will be referred to as J. The final curve is shown in figure 4, each plotted point representing data obtained from a single iron line.

<sup>12</sup> Slavin, M., Iron Arc as a Standard Source for spectrochemical Analyses: Jour. Ind. Eng. Chem., vol. 12, 1940, p. 131.

<sup>13</sup> Sherman, J., and Jenkins, J. W., A Review of Spectrographic Analysis of Some Metals and Alloys: American Society of Naval Engineers vol. 55, 1943, p. 189.

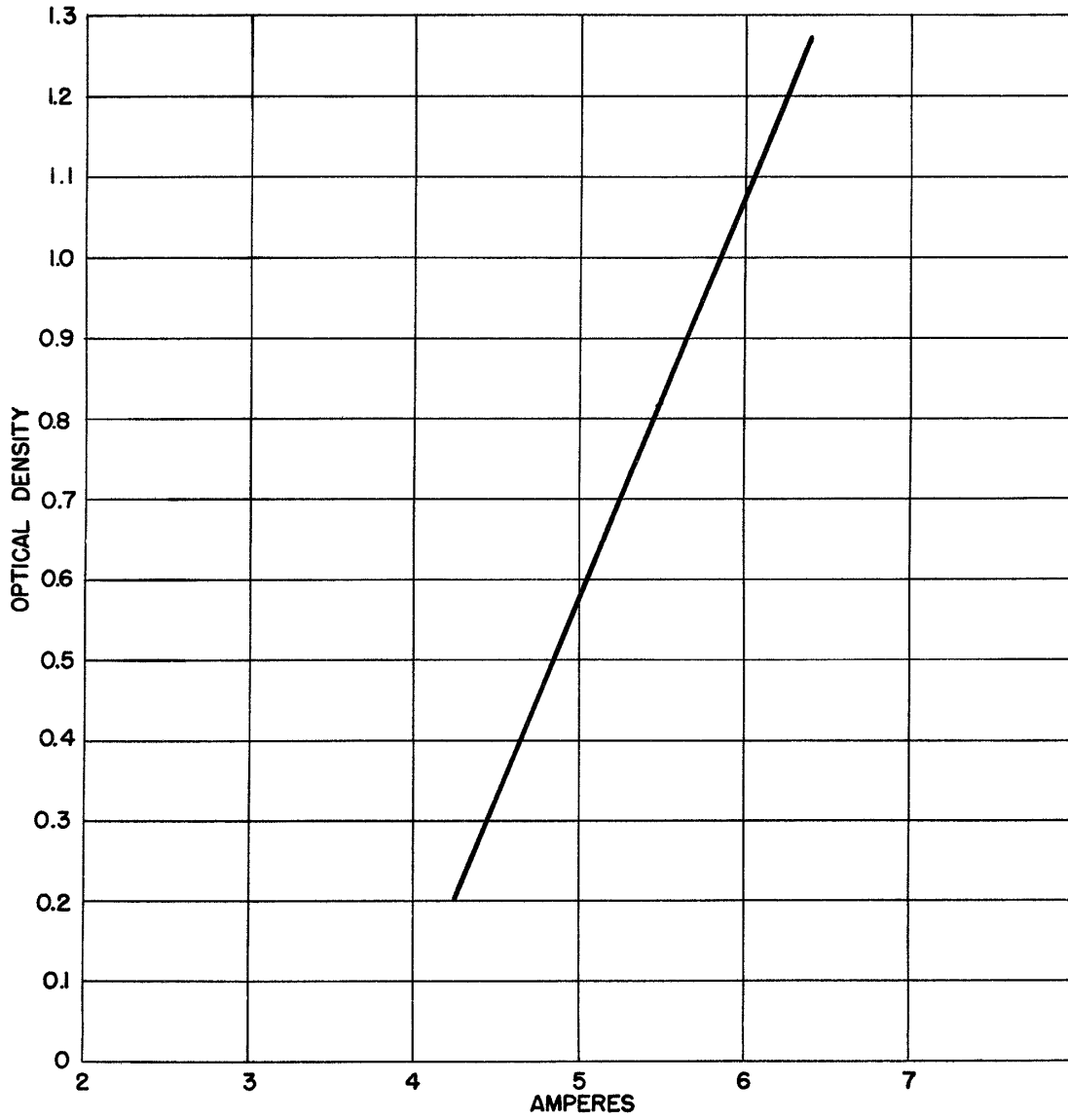


Figure 2. - Variation of density of blackening with excitation current,  
Fe  $\lambda$  3091.598 Å.

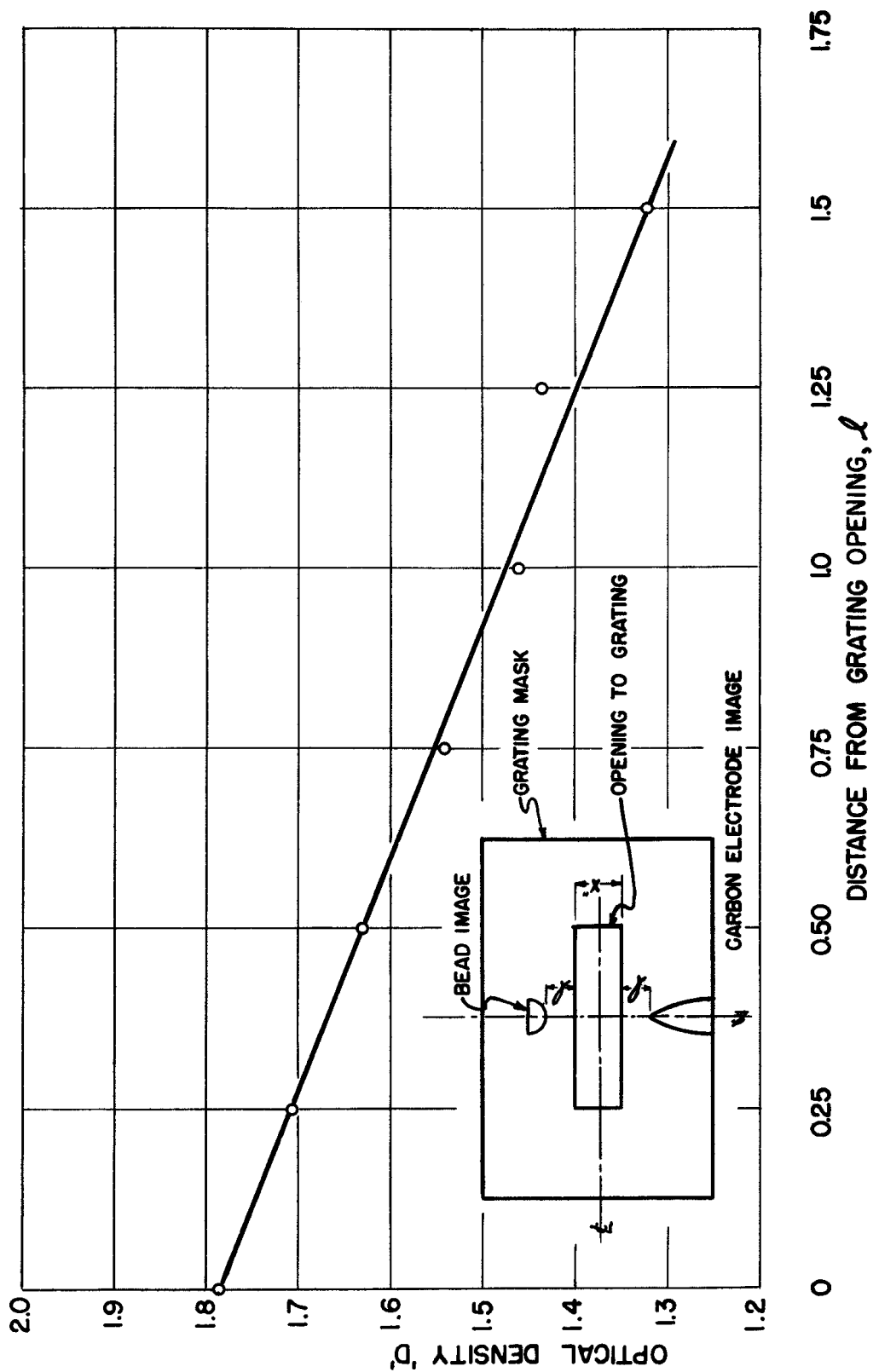


Figure 3. - Change in optical density of the iron line Fe  $\lambda$  3091.6 A with image position.

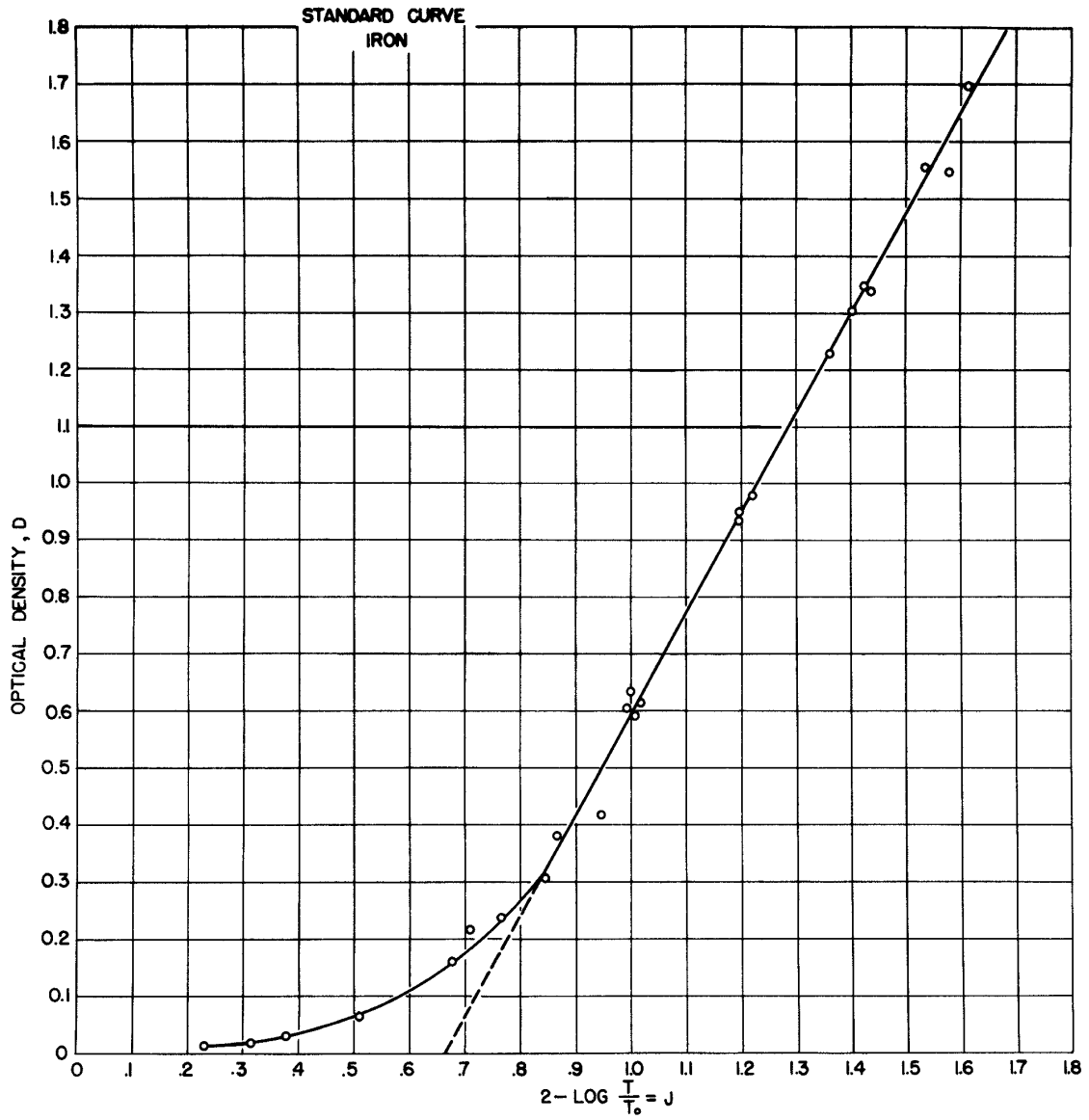


Figure 4. - Plate-calibration curve.

In subsequent plate calibrations, it is only necessary to use a rotating sector having a total aperture of 45° and expose for 120 seconds. It would be possible to expose for 15 seconds without a step sector, but the former procedure is better, as the variations resulting from the slight fluctuations in the arc are smoothed out somewhat. After processing the plate, the densities of the same iron lines are measured and plotted against their corresponding  $I$  values obtained previously.

The advantage of this method is that the length of the iron lines in the standard need be no greater than 1/8 inch; as many as 23 spectrograms can be taken on a 4 by 10 inch plate.

The optical densities of chosen lines are measured for the standards or for the sample being analyzed.  $I$  values for these optical densities are read from the calibration curve. In the preparation of standards,  $I$  values for a particular spectral line are plotted against the corresponding logarithms of the masses of the element volatilized in the arc, and a standard curve is thus obtained.

### PREPARATION OF STANDARD CURVES

A standard curve is a plot of the optical density relative intensity, or other function of light intensity for a particular spectral line versus the logarithm of the mass of the element volatilized in the arc. Such a curve is used in subsequent analyses of unknown samples for the element.

Five steps are involved in the preparation of standard curves to be used for quantitative determinations:

1. Compounds containing the desired elements are weighed and ground with weighed amounts of the diluting agents. Spectrographic graphite powder of known purity is nearly always included. It has been found that the addition of graphite causes the arc to burn more smoothly and helps prevent the coalescence of molten droplets. If such droplets form a bead, the arc sometimes strikes to the carbon rather than to the bead, and after the electrode pit has burned away, the bead rolls off the electrode with consequent loss of material. This is particularly true of refractory oxides such as alumina, magnesia, etc.

The ingredients are ground together in a mechanical mortar until the mixture is homogeneous. The time of grinding required to obtain homogeneity depends not only on the amount of material to be ground but also on certain physical properties of the substances entering into the mixture. Several hours are generally sufficient. The total weight of the mixtures which we have prepared was usually less than 8 grams.

2. A series of samples of the ground mixture is weighed out and each sample placed in a shallow pit in the end of a 3/16 inch-diameter carbon electrode. It is necessary to use a good microbalance which weighs accurately to  $10^{-5}$  grams. Weights of complex range from 0.008 to 6 milligrams, or higher, depending on concentration in the matrix and intensity of the line chose. After transferring by means of a brush and a small funnel to the electrode, the sample is packed down tightly with a hardened alloy steel rod. Particular care must be taken to see that all of each sample is transferred.

3. The samples are burned in the d.c. arc under controlled optical and electrical conditions, and spectrogram of each is taken. The lower electrode containing the sample is made positive; the upper electrode is a 1/8 inch spectrographic carbon (fig. 1). The position and separation of the electrodes is determined by means of a rule mounted vertically and carrying a slide with horizontal pins. It is mounted on the optical bench, so that it can be swung into position readily.

In general, the volatilization period is less than 2 minutes for samples lying in the usual weight range. It is important that the current be maintained as constant as possible during the volatilization period. A current of 4 amperes and an electrode separation of 5.5 millimeters were found satisfactory for general work. The current was controlled manually by means of a rheostat. Later an electronic current regulator constructed in this laboratory was employed, but it was not available when the work on germanium, tin, and lead was done.

The distance of each electrode from the horizontal plane of symmetry of the grating should be kept constant.

4. After processing the plate, the densities of selected lines in the spectrum of the element for which standards are to be prepared are measured by a recording microdensitometer.<sup>14</sup> Nearly any line can be used if its density is in the range for which the standard is being prepared. For very low concentrations,

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<sup>14</sup> Machler, R. C., A New Recording Microphotometer: Proceedings, Seventh Summer Conference on Spectroscopy and its Applications: John Wiley & Sons, Inc., New York, 1940.

it is necessary to use the most persistent lines. These lines often show self-reversal, but this is usually not an important factor when the vapor concentration in the arc is low.

Occasionally the position of certain spectral lines of an element fall in the same position on the photographic plate as the most persistent line or lines of another element being determined, particularly if the former is a major constituent of a sample and an element of high atomic number. The element most likely to produce such masking effects is iron, as it is found in nearly all ore samples and yields many lines in the ultraviolet region. Masking effects can, in part, be obviated by using a spectrograph of high dispersion and resolution.

5. Density data are expressed in terms of relative intensities. Curves are drawn showing the variation of the relative intensity or optical density of a given line with the logarithm of the mass of the element in the burned sample. Thus, standard curves are obtained from which the amount of an element required to give a certain relative intensity of spectral line can be obtained.

It is observed (fig. 8) that these curves are not linear throughout but approach the axis of abscissas tangentially. This is a result of the sigmoid response of the photographic plate and is not inherent in the atomic excitation occurring in the arc. The reason that  $\log_{10} m$  can be plotted instead of  $\log_{10} L$  is because of the relationship

$$\log_{10} \gamma = C \log_{10} L$$

where  $L$  is the total illumination for a particular spectral line when a sample containing a given element is completely burned in the arc,  $C$  is a proportionately constant, and  $\gamma$  is the mass in units of  $10^{-6}$  gram.

To aid in preventing errors resulting from differences in emulsions, a group of Eastman Spectrum Analysis No. 1 plates, all having the same emulsion number was used. All plates were brush-developed for 5 minutes at  $18^{\circ}$  C. in D-19 developer.

#### SOURCE OF ERROR

The sources of error in the total-energy method are as follows:

1. Variations in the emulsions of the photographic plates. This is partly eliminated by putting an iron spectrogram on each plate as well as the standard plates, using the Pfund arc so that variations in line density due to the emulsions can be determined and corrections made. There may be local variations in the emulsion, however, which are too small in extent to be corrected in this way and must be included with other errors in determining the overall accuracy of the method. This error should not exceed 3 percent, however, as the plates are guaranteed by the manufacturer to be uniform within this limit.

2. Inaccuracies in weighing samples. If a good microbalance is used with care, these are small, unless extremely small samples are employed.

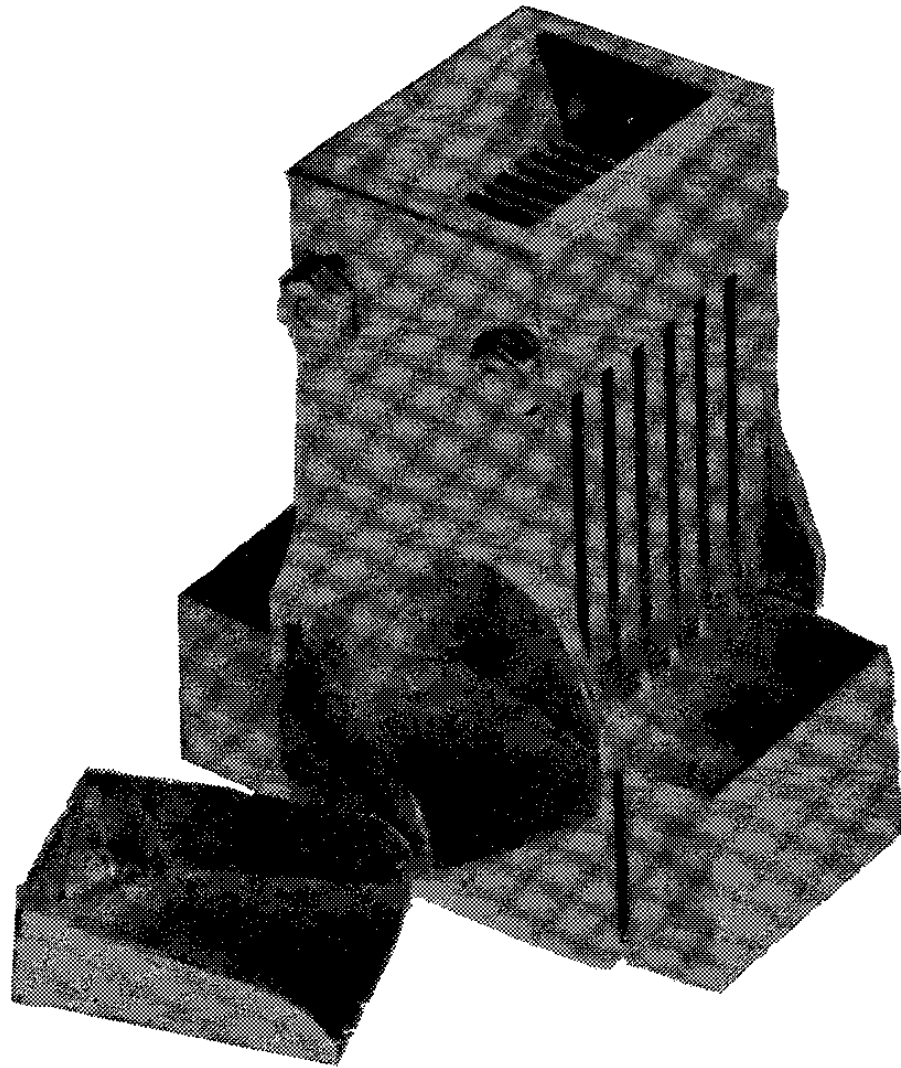
3. Unsteadiness of the a.c. arc during the volatilization period. Manual control by a rheostat is not very satisfactory, as rapid variations are not indicated by the ammeter and human reaction time is too slow. Marked improvement can be obtained by electronic or magnetic current control. As no reference line is used, as in the internal standard method, corrections are not made for variations resulting from the behavior of the arc. At present, the total energy method has neither the accuracy nor the reproducibility of the internal standard method.

4. Influence of extraneous elements on line intensities. This was discussed.

5. Sampling. Usually only 0.01 gram of sample or less is employed, so that sampling must be done with great care. Grinding to minus 200-mesh is generally sufficient. A small splitter, which is useful for proper sampling, is shown in figure 2. An attempt is being made to develop methods for using larger samples.

6. Presence of impurities in spectroscopic carbons. Germanium, tin, and lead have not been found in any of the carbons used. The carbons commercially obtainable for general work contain traces of iron, aluminum, boron, silicon, magnesium, and sometimes other elements. The distribution of these impurities is usually not uniform along the length of the rods, so that no adequate correction can be made for them. It is possible, however, to treat these carbons in the laboratory and thus remove most of the impurities.

7. Measurement of the optical density of a spectral line. The source of error in this instance does not reside to any extent in the densitometer, as very good instruments can be constructed or purchased. The chief source of error lies in determining the proper correction for background density if it is present. Images of spectral lines on photographic films or plates can be classified into five types, which are



**Figure 5. - Small sampling device.**

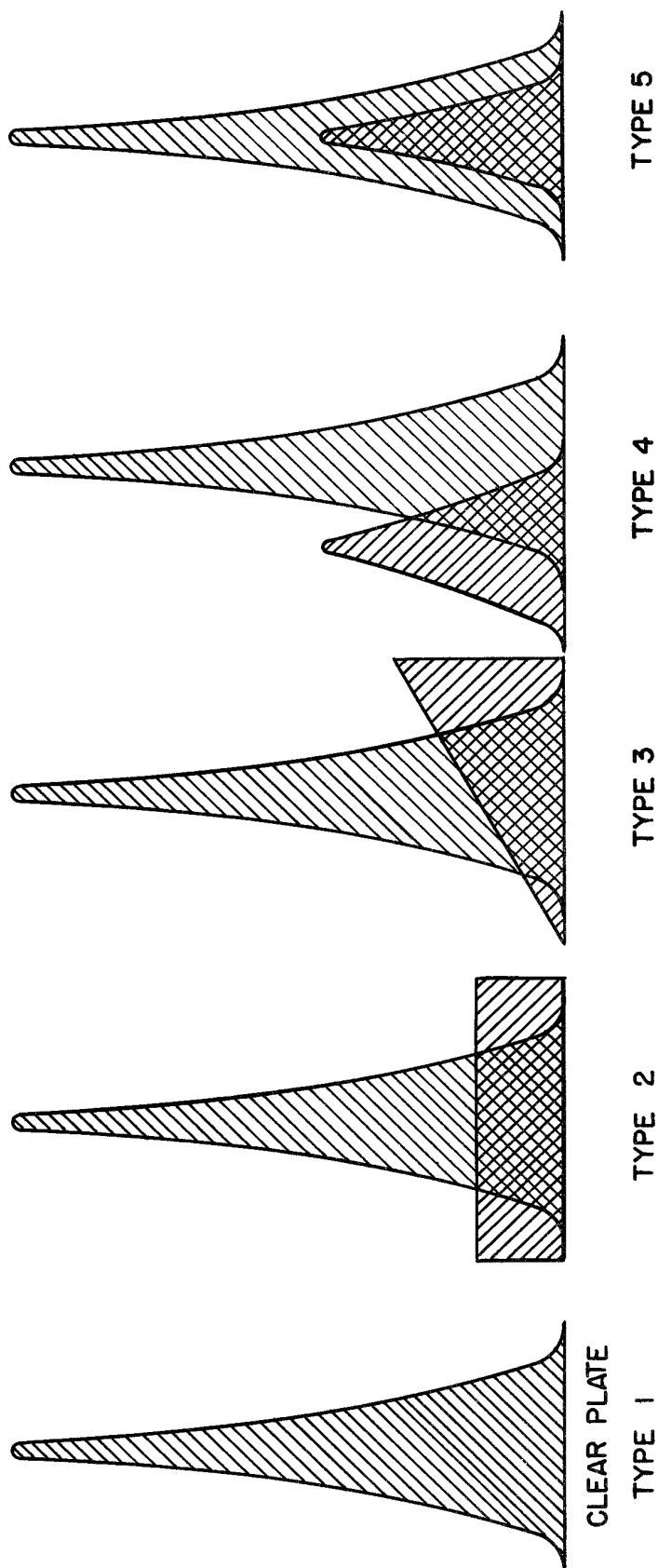


Figure 6. - Schematic representation of images of spectral lines and background occurring on negative spectrograms.



represented schematically in figure 6. In the ideal case, type 1, there is no background, and the line stands out sharply against the clear plate. The only error results from the inaccuracy of the densitometer. In type 2, correction can be made readily, provided the optical density of the background is considerably less than that of the spectral line. The densitometer zero is adjusted for clear plate, and the optical densities of the background and spectral line may then be determined. The background density is converted to relative intensity by means of the plate calibration curve and subtracting this value from the corresponding intensity for the spectral line. Incorrect results are obtained if the zero of the densitometer is adjusted to correspond to the background density and the line density then measured, unless the background density is less than about 0.01. In type 3, where the background density is somewhat higher on one side of the line than on the other, the difference on the two sides is usually not serious, and correction can be made as described above. If desired, a mean value can be obtained and used. Type 4, in which two spectral lines are not completely resolved, sometimes yields difficulties. Type 5 is uncorrectable and means that one line is masked by another.

## TIN

### Effect of Certain Extraneous Elements upon the Intensities of Tin Lines

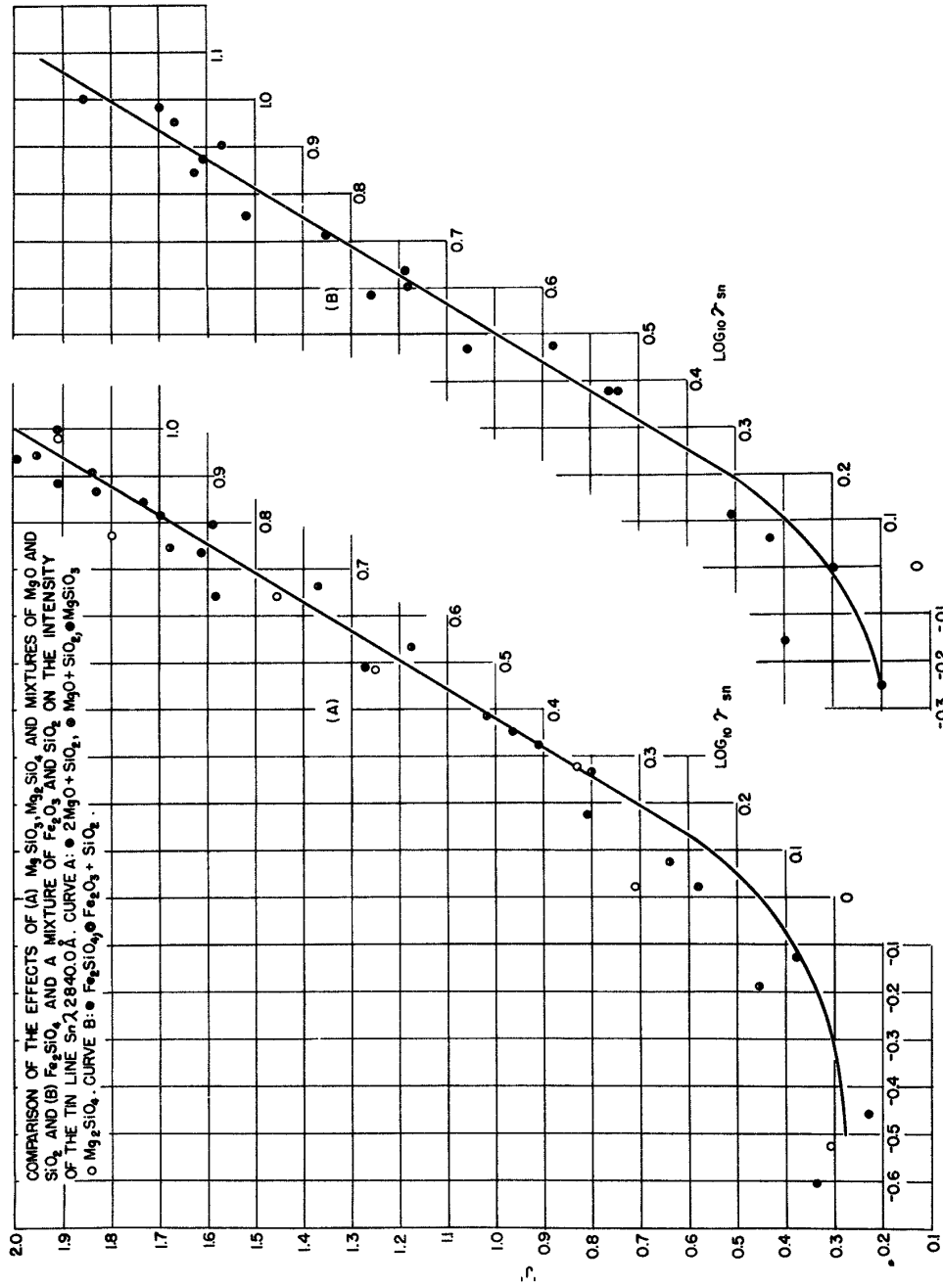
The most persistent tin line (U1) listed in Harrison's tables<sup>15</sup> is Sn 2839.989 Å. It is sufficiently resolved from the iron line Fe  $\Lambda$  2840.423 Å to eliminate masking errors. Other intense lines in the ultraviolet region, which might be useful under certain conditions are Sn  $\Lambda\Lambda$  2863.327, 3173.019, and 3262.328 Å. The tin line Sn  $\Lambda$  3262.328 Å can be seriously masked by the iron lines Fe  $\Lambda$  3262.280 and  $\Lambda$  3262.013 Å, however.

In investigating the effects of extraneous elements upon the intensities of tin lines, it would be simplest to use mixtures of oxides. The question arose whether or not mixtures of oxides with silica would have the same effects upon line intensities as do the corresponding silicates. Mixtures were prepared, each of which contained one-third graphite by weight and 0.5 percent tin as SnO<sub>2</sub> and the following base materials, respectively: (a) Synthetic enstatite, MgSiO<sub>3</sub>; (b) MgO and SiO<sub>2</sub> in stoichiometric proportions of 1:1; (c) synthetic forsterite, Mg<sub>2</sub>SiO<sub>4</sub>; and (d) MgO and SiO<sub>2</sub> in stoichiometric proportions of 2:1. Samples of each mixture were weighed out, and data were obtained by the method previously described. The results shown in curve A, figure 7, indicate that no difference in line density greater than experimental error is found between these silicates and the corresponding oxide mixtures. Previous chemical combination has no influence. As the mol fraction of MgO in Mg<sub>2</sub>SiO<sub>4</sub> is twice what it is in MgSiO<sub>3</sub>, it might have been expected that a difference in effect on line intensity would have resulted. However, none was observed. More will be said later concerning this observation. Similar investigations were made with synthetic fayalite, Fe<sub>2</sub>SiO<sub>4</sub> and mixtures of Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in 1:1 proportions, oxygen and the difference between the ferrous and ferric condition having been ignored. These mixtures also contained one-third graphite by weight and 0.5 percent tin as SnO<sub>2</sub>. Again, no differences beyond those due to experimental error, were observed. The synthetic silicates were prepared by the methods described by Kelley.<sup>16</sup>

It was desirable to know whether or not the time of volatilization of tin from ore samples is markedly different from that from synthetic mixtures under identical excitation condition in the arc. If differences in rates of volatilization occur, relative concentrations in the arc during the burning period would be different. Thus, effects upon line intensities might not be the same, even though the analytical composition with respect to the constituents is identical, and studies made with oxide mixtures might not then be pertinent. To verify this, an ore containing 0.32 percent tin by chemical analysis was diluted so that the mixture contained 37 percent graphite. The tin was present as cassiterite in a tourmalinized, brecciated, rhyolite porphyry. A series of samples of equal weight was burned, each for a prescribed interval, under the previously stated controlled conditions, and spectrograms were taken. The same procedure was followed in studying a mixture of Fe<sub>2</sub>O<sub>3</sub>, graphite, and 0.5 percent tin as SnO<sub>2</sub>. The weights

<sup>15</sup> Harrison, G. R., Massachusetts Institute of Technology Wavelength Tables: John Wiley & Sons, Inc., New York, 1939.

<sup>16</sup> Kelley, K. K., The Specific Heats at Low Temperatures of Ferrous Silicate, Manganous Silicate, and Zirconium Silicate: Jour. Am. Chem. Soc., vol. 63, 1941, p. 2750.  
Kelley, K. K., Specific Heats at Low Temperatures of Magnesium Orthosilicate and Magnesium Metasilicate: Jour. Am. Chem. Soc., vol. 65, 1943, p. 339.



o Figure 7. - Comparison of the effects of (a)  $MgSiO_3$ ,  $Mg_2SiO_4$  and mixtures of  $MgO$  and  $SiO_2$  and (b)  $Fe_2SiO_4$  and a mixture of  $Fe_2O_3$  and  $SiO_2$  upon the intensity of the tin line  $Sn \lambda 2840.0 \text{ \AA}$ . Curve A:  $\bullet$   $MgO + SiO_2$ ,  $\circ$   $MgSiO_3$   $\circ$   $Mg_2SiO_4$ . Curve B:  $\bullet$   $Fe_2SiO_4$ ,  $\circ$   $Fe_2O_3 + SiO_2$ .

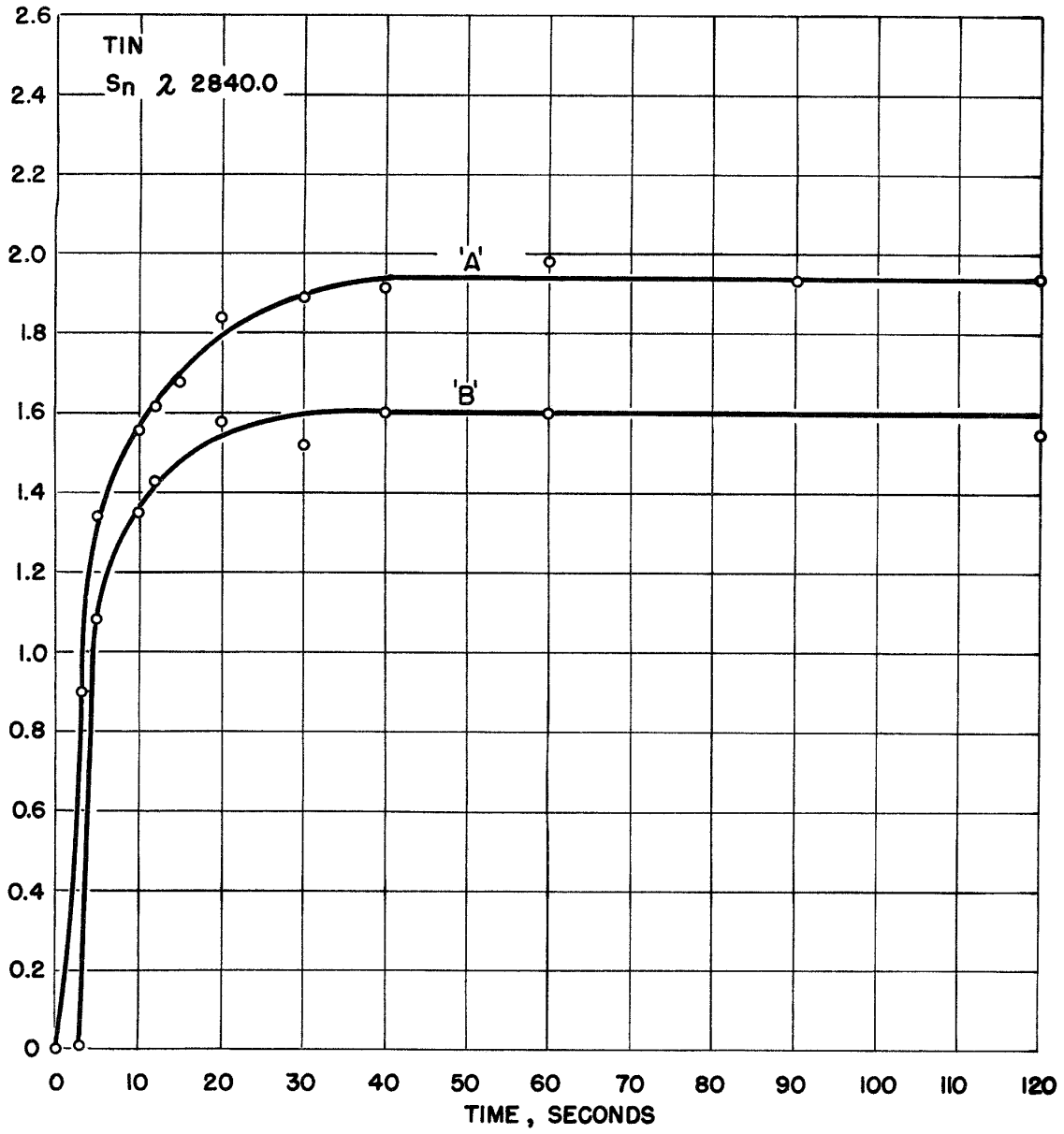


Figure 8. - Time of volatilization of tin from (a) an ore sample containing cassiterite and (b) a sample containing SnO<sub>2</sub> in Fe<sub>2</sub>O<sub>3</sub>.

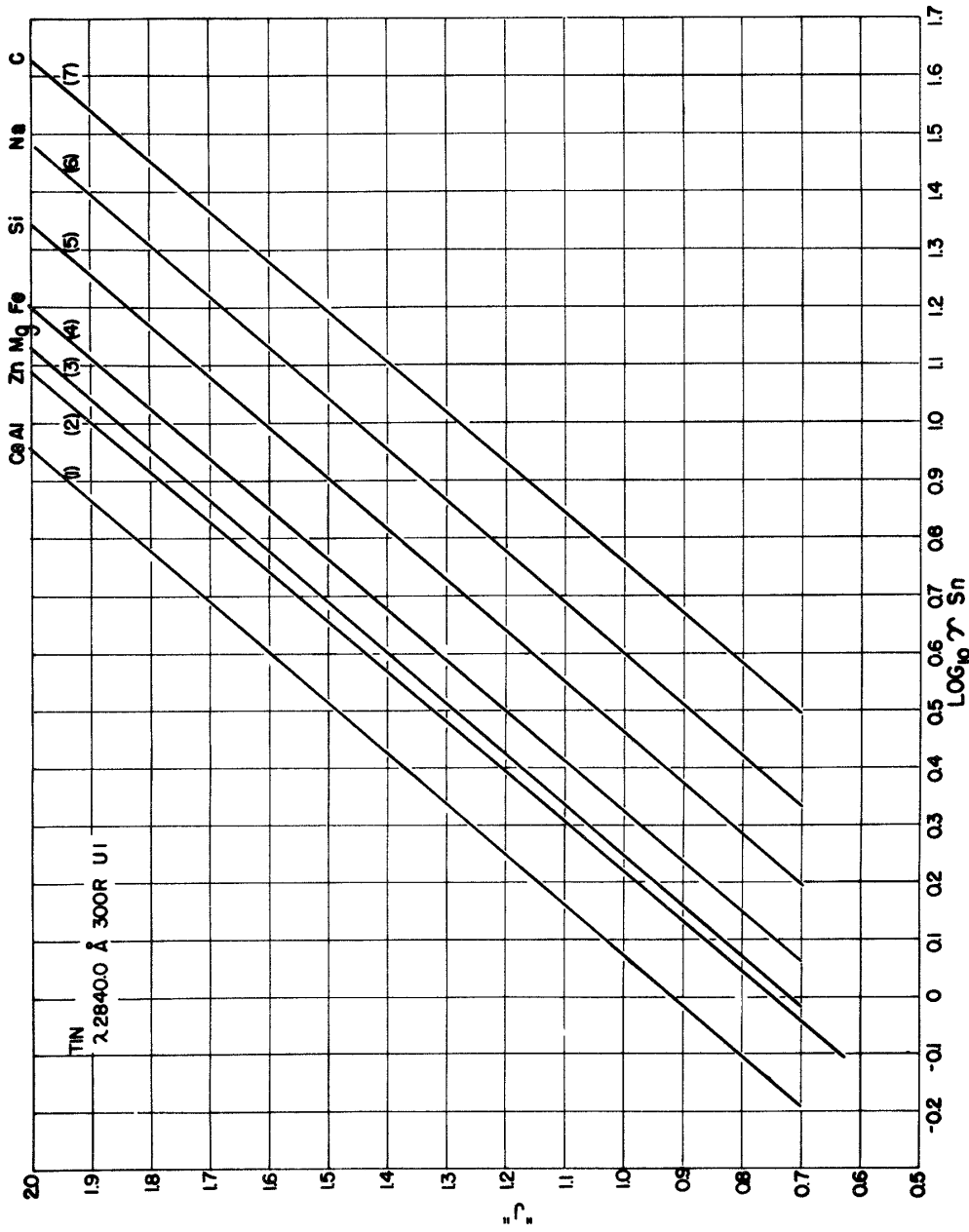


Figure 9. - Standard curves showing the effects of extraneous elements upon the intensity of the tin line Sn 2840.0 Å. Curve (1), CaO, Al<sub>2</sub>O<sub>3</sub>; (2) ZnO; (3) MgO; (4) Fe<sub>2</sub>O<sub>3</sub>; (5) SiO<sub>2</sub>; (6) NaCl; and (7) graphite.

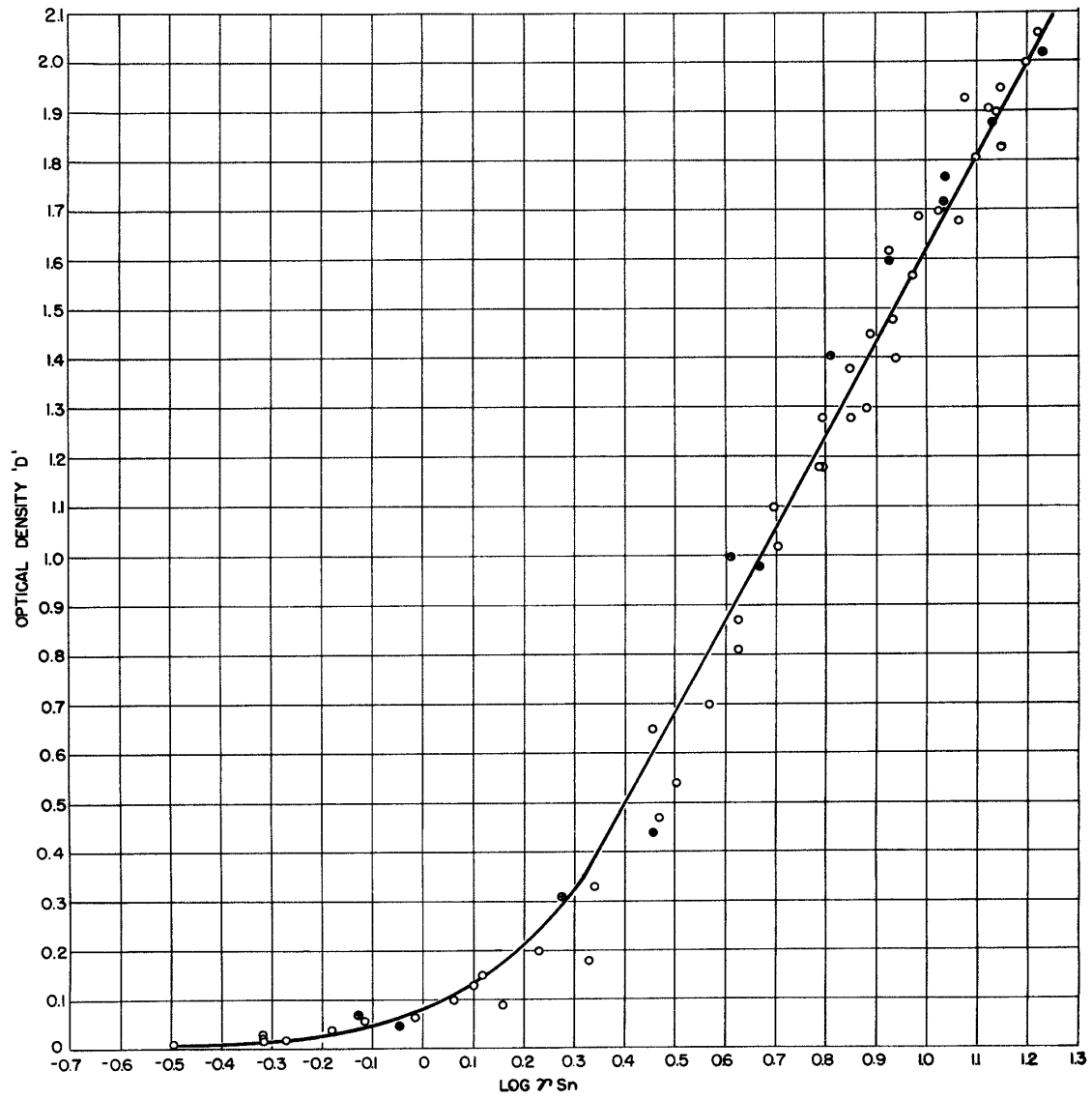


Figure 10. - Representative optical density,  $D$ , versus  $\log \tau$  curve for the tin line  $\lambda 2840.0 \text{ \AA}$ ,  $\circ$  SnO in  $\text{SiO}_2$ ;  $\otimes$  SnO<sub>2</sub> in  $\text{SiO}_2$ ;  $\bullet$  Sn metal in  $\text{SiO}_2$ .

of tin in the sample of the two series were identical. From figure 8 it is evident that the rates of volatilization of tin from the ore and iron oxide mixtures were approximately the same. The difference in position of the two curves is due to the effect of the matrices upon the density of the tin line.

Following the above, the effects of Ca, Al, Mg, Fe, Si, Zn, Na, and K upon the intensities of the previously mentioned tin lines with particular reference to Sn  $\Lambda$  2840.0 Å. Data concerning the various mixtures are given in table 1. Results are plotted in figure 9 and will be discussed later. The mol fraction of graphite added to each mixture was about the minimum necessary to prevent the coalescence of the charge with subsequent loss. All base materials employed were examined spectrographically before use and were found to be free of tin.  $\text{CaCO}_3$  and  $\text{MgCO}_3$  were used rather than the oxides, because the latter are hygroscopic, there being no reason for believing that the carbonates would behave differently than the corresponding oxides. Studies were made with metallic Sn, SnO, and SnO<sub>2</sub> as sources of tin, but no differences in line intensity were observed other than those due to experimental error. These results are shown in figure 10. Mixtures were prepared in the natural minerals aragonite and amphibole and in magnesium trisilicate, analyses of which are given in table 1. The aragonite contained nearly 50 percent CaO; the same standard curve was obtained as when  $\text{CaCO}_3$  was used as a matrix. The amphibole and magnesium trisilicate were high in silica; results were the same as when pure silica was employed.

Standard curves showing the effects of Al, Ca, Zn, Mg, Fe, Si, and Na on the intensity of the tin line Sn  $\Lambda$  2840.0 Å are presented in figure 9. CaO and Al<sub>2</sub>O<sub>3</sub> had the same effect upon the intensity of Sn  $\Lambda$  2840.0 Å. In the presence of the other base materials, the intensity of this tin line was relatively less. Silicon and sodium had a particularly marked effect. It is seen that when graphite alone was the matrix, the intensity was the lowest of all. Another interpretation of the results is that the intensity of this tin line was enhanced, relative to its intensity in graphite, by the addition of extraneous elements. Graphite of course was simultaneously burned in all instances.

The effect upon the accuracy of an analysis of this change in density with various matrices can be seen from the following examples: Let us consider as a hypothetical case, a sample weighing 5 milligrams that contains tin and that has been burned in the arc and a spectrogram taken under controlled conditions identical with those used in preparing the standards. If  $\int$  is 1.5, then the following percentages of tin are obtained, using the curves in order from left to right (fig. 9): 0.07, 0.09, 0.10, 0.11, 0.16, 0.22, and 0.31. If 0.07 percent represents the correct result, it is seen that the error, based upon a standard prepared in graphite, is of the order of 450 percent.

As sodium and potassium are known to reduce markedly the line intensities of many elements, the effects of these alkali metals were investigated. Standards were prepared with NaCl, KCl, and K<sub>2</sub>CO<sub>3</sub>, respectively, as matrices. The data obtained with the potassium salts were too erratic to yield an accurate curve. However, they did show that the intensity of the tin line was reduced markedly, just as it was when sodium was employed.

Data were also obtained on the tin lines Sn  $\Lambda\Lambda$  2863.3, 3173.0, and 3262.3 Å at the same time as on the tin line Sn  $\Lambda$  2840.0 Å, except when iron oxide was used as the base material. The shifts of the standard curves were in the same order with respect to the base materials as with the line Sn  $\Lambda$  2840.0 Å.

Among the factors that may determine the intensity of a given tin line in the arc are the relative concentrations of the extraneous element with respect to tin in the arc. Concentrations no doubt affect energy distribution, and thus the energy in the arc may be taken in the excitation of one element at the expense of the other, thus lowering the intensities of certain wave lengths of the latter. Low ionization potentials mean low energies of excitation. No simple relationships are to be expected, but trends can be indicated.

In figure 11, values of the first ionization potential<sup>17</sup> of the metal atom in the extraneous material are plotted against the values of the logarithm of the weight of tin required to yield an intensity corresponding to a  $\int$  value of 1.5 for Sn  $\Lambda$  2840.0 Å. The latter data were obtained from the standard curves of figure 7. The general trend follows in order, but there are exceptions: sodium and potassium (not shown), which have low first ionization potentials, markedly reduce the intensity of the tin line.

<sup>17</sup> Backer, R. F., and Goudsmit, S., Atomic Energy States: McGraw-Hill Book Co., Inc., New York, 1932.

Very rough estimates of the vapor pressures in atmospheres at 2,000° C. for  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  were obtained by use of the equations in Kelley's bulletin.<sup>18</sup> Logarithms of these values are plotted against the weight of tin required to yield a  $J$  value of 1.5 in figure 12. The general trend is that, as

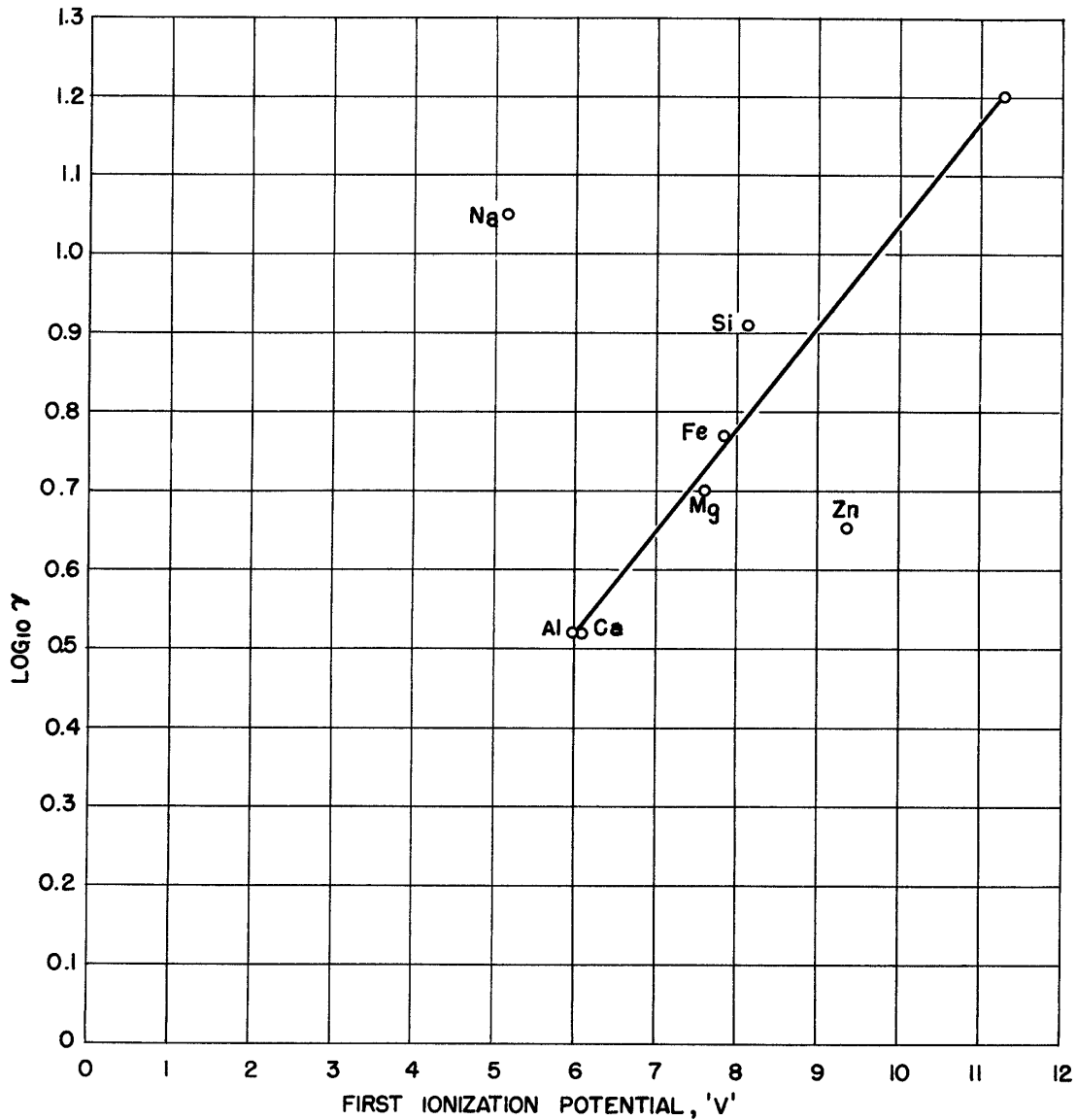


Figure 11. - Variation of the weight of tin required to yield a fixed line intensity for Sn,  $\lambda 2840.0 \text{ \AA}$  with the first ionization potential.

<sup>18</sup> Kelley, K. K., Contributions to the Data on Theoretical Metallurgy, III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances: Bureau of Mines Bull. 383, 1935, 132 pp.

Table 1  
Data concerning various mixtures employed in studying effects of extraneous elements upon the intensities of tin lines

Matrix	Ca CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgCO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	ZnO	Graphite	NaCl	Argonite	Magnesium Trisilicate	Amphibole
Mol fraction											
Matrix to Graphite . . .	1:3	1:5	1:2	1:2	1:3	1:1	--	1:1	75 percent aragonite	62.5 percent silicate	75 percent amphibole
Sn, mg. per grams of mixture . . .	5.67	4.97	5.21	5.09	5.96	--	--	--	--	--	--
SnO <sub>2</sub> , mg. per grams of mixture . . .	5.57 5.84	5.86 --	5.09 5.48	5.25 --	5.47 5.34	-- --	5.13 5.80	-- --	5.58 5.37	-- --	-- 5.41
SnO <sub>2</sub> , mg. per grams of mixture . . .	6.06	5.30	5.74	5.71	4.94	5.61	--	5.58	--	5.26	--
Curve number in figure 7	1	1	3	4	5	2	7	6	1	5	5



	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
Amphibole .....	47.4	14.3	14.7	3.40	13.00
Aragonite .....	5.2	49.3	.1	.45	.43
Magnesium .....	--	--	--	--	--
Trisilicate .....	51.0	--	22.5	--	--

Tin is vaporized rapidly and Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO more slowly than Fe, SiO<sub>2</sub> and NaAl, the latter group have the more marked effect in reducing line intensity. No doubt it would be better to use boiling points, as those are probably the temperatures of the pure materials in the arc, but such data are not available.

As the gangue of an ore sample generally will consist of several minerals (often largely complex silicates), each affecting line intensities, the effects of mixtures of oxides or carbonates with or without silica were investigated.

As the intensities of tin lines in the ultraviolet spectral region are markedly less in the presence of silicon than in the presence of aluminum or calcium, the effects of various mixtures of these elements, using CaCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> as sources, upon the intensity of the tin line Sn  $\Lambda$  2840.0 Å were investigated. Primary mixtures of each of these three compounds, having the same mol fractions of graphite as previously mentioned and containing 0.500 milligram of tin as SnO<sub>2</sub> per gram of sample, were prepared. Then, from these mixtures others were made by weighing out desired amounts of each and subsequently grinding them mechanically. Composition of the mixtures in percentage by weight was calculated in terms of the oxides CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, the graphite (CO<sub>2</sub>) and small percentage of tin being ignored. As the percentage tin in the three original mixtures was the same, it likewise was the same in all subsequent mixtures prepared therefrom, and any change in intensity can be ascribed to the effect of extraneous elements. Hereafter, a matrix containing two primary constituents, for example CaO and SiO<sub>2</sub>, will be referred to as bi-constituent diluent, one containing three, a tri-constituent diluent, etc.

Series of bi-constituent mixtures of CaO and SiO<sub>2</sub>, CaO and Al<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were prepared. Each series ranged from 0 to 100 percent for both constituents, the steps being 5 to 10 percent intervals. Samples weighing 0.70 milligram, each containing 3.5 gamma of tin, were burned in the arc under the previously described controlled conditions, and spectrograms were taken. At least four samples of each mixture were run. After plate processing, the optical densities were determined for the line Sn  $\Lambda$  2840.0 Å. Mean values of optical densities were calculated for each mixture.

The results are represented by means of a triangular space diagram shown in figure 13. This diagram should not be confused with the ordinary three-component phase chart. Percentage composition of the bi-constituent mixtures containing CaO and SiO<sub>2</sub> is resented along the edge of the triangle, that of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and that of CaO and Al<sub>2</sub>O<sub>3</sub> along the other two, respectively. Any internal point represents a mixture containing all three constituents. The optical densities for the line Sn  $\Lambda$  2840.0 Å for particular matrix compositions are plotted vertically. Optical densities were used for representation rather than values of  $\int$  because differences are then a little more marked.

Data for two tie lines corresponding to 50 percent silica and a perpendicular dropped from the 100 percent silica vertex to the 50 percent Al<sub>2</sub>O<sub>3</sub>, 50 percent CaO point were obtained. In the latter mixtures, the percentages of Al<sub>2</sub>O<sub>3</sub> and CaO were the same in any given sample but their sum varied from point to point. It is observed that when the percentage of SiO<sub>2</sub> is less than 50, no marked effect upon line intensity results.

Investigations concerning the effects upon line intensity of other mixtures also were made. In figure 14 are plotted values of  $\int$  for the same tin line for the bi-constituent system MgO-SiO<sub>2</sub>. MgCO<sub>3</sub> was employed. SiO<sub>2</sub> in small percentages has a marked effect in reducing line intensity. It is to be noted that  $\int$  values for a stoichiometric mixture 1MgO:1SiO<sub>2</sub> containing 40.2 percent MgO and a stoichiometric mixture 2MgO:1SiO<sub>2</sub> containing 57.3 percent MgO would be the same. This corresponds to the previously discussed results illustrated in figure 7.

Further studies were made concerning sodium and potassium. Primary mixtures containing Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> in the mol ratio 1:1 and, respectively, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, were prepared. Each contained 0.5

percent tin as  $\text{SnO}_2$ . Graphite was present in the mol ratios with respect to  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  as in previous work (table 1). The graphite in the  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  mixtures was in a 1:1 mol ratio. Two series of

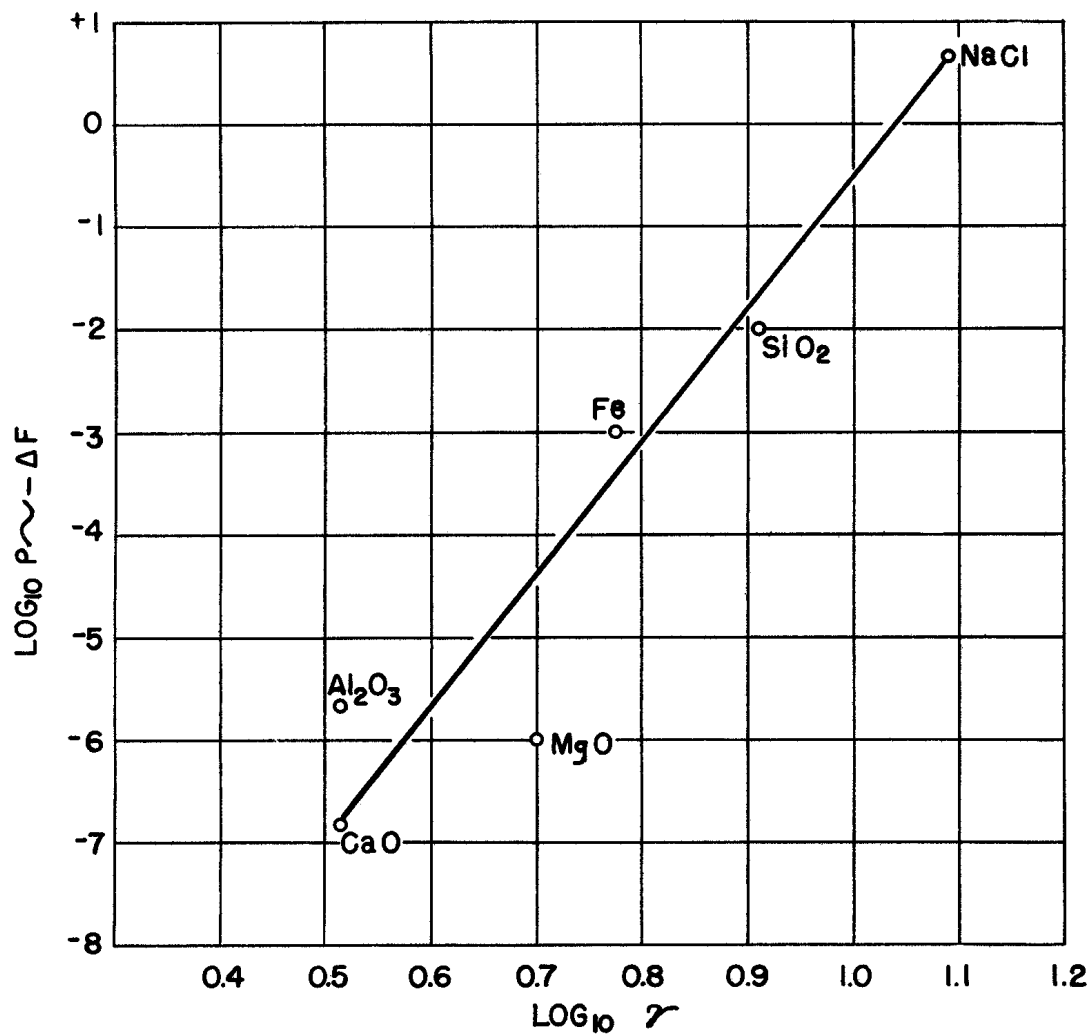


Figure 12. - Variation of the weight of tin required to yield a fixed line intensity for Sn  $\lambda 2840.0 \text{ \AA}$  with the logarithm of the vapor pressure in atmospheres (proportional to the free energy of vaporization at 2,000 K.)

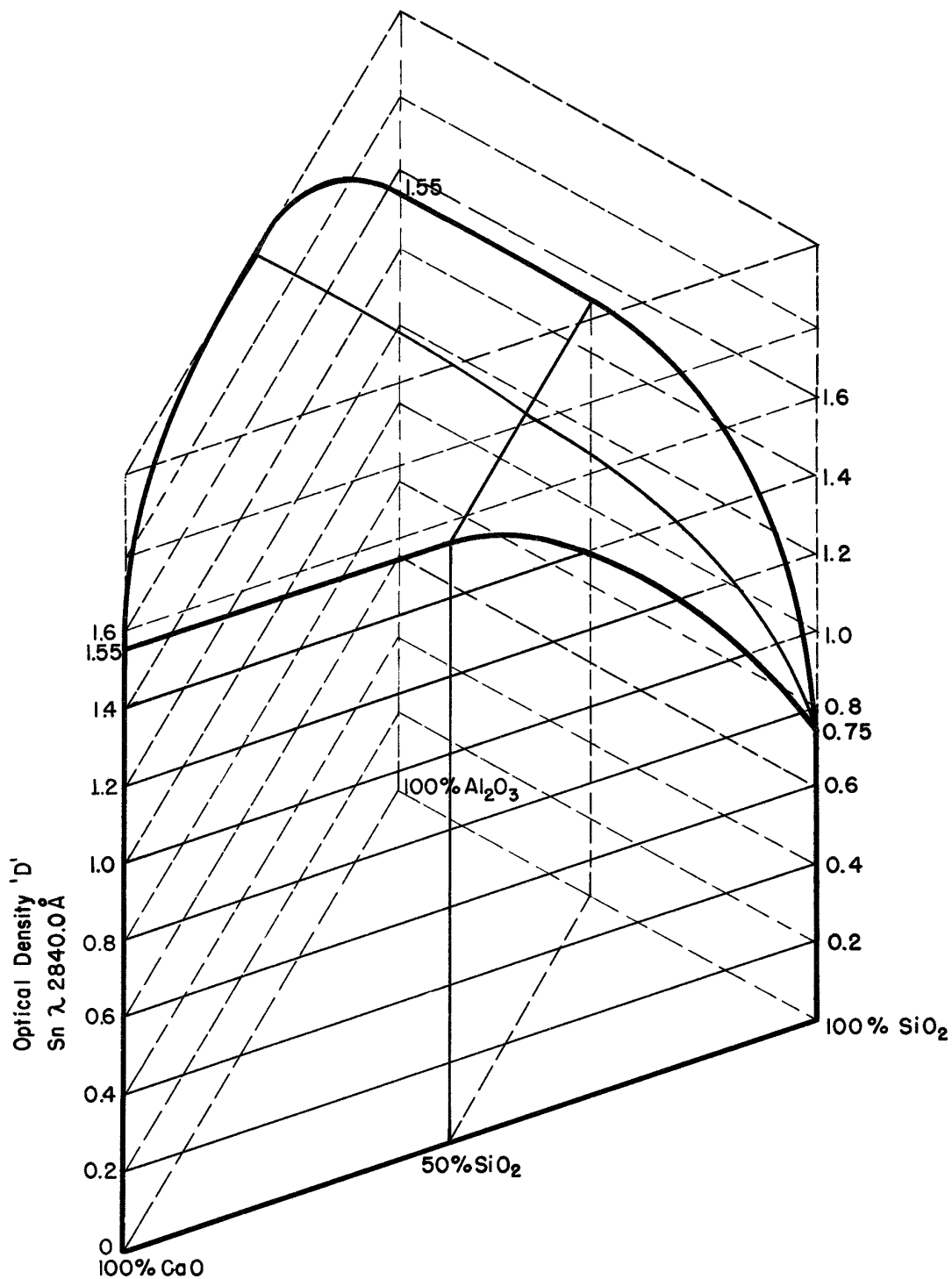


Figure 13. - Triangular space diagram showing the effect of CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and mixtures thereof upon the optical density of Sn λ 2840.0 Å.

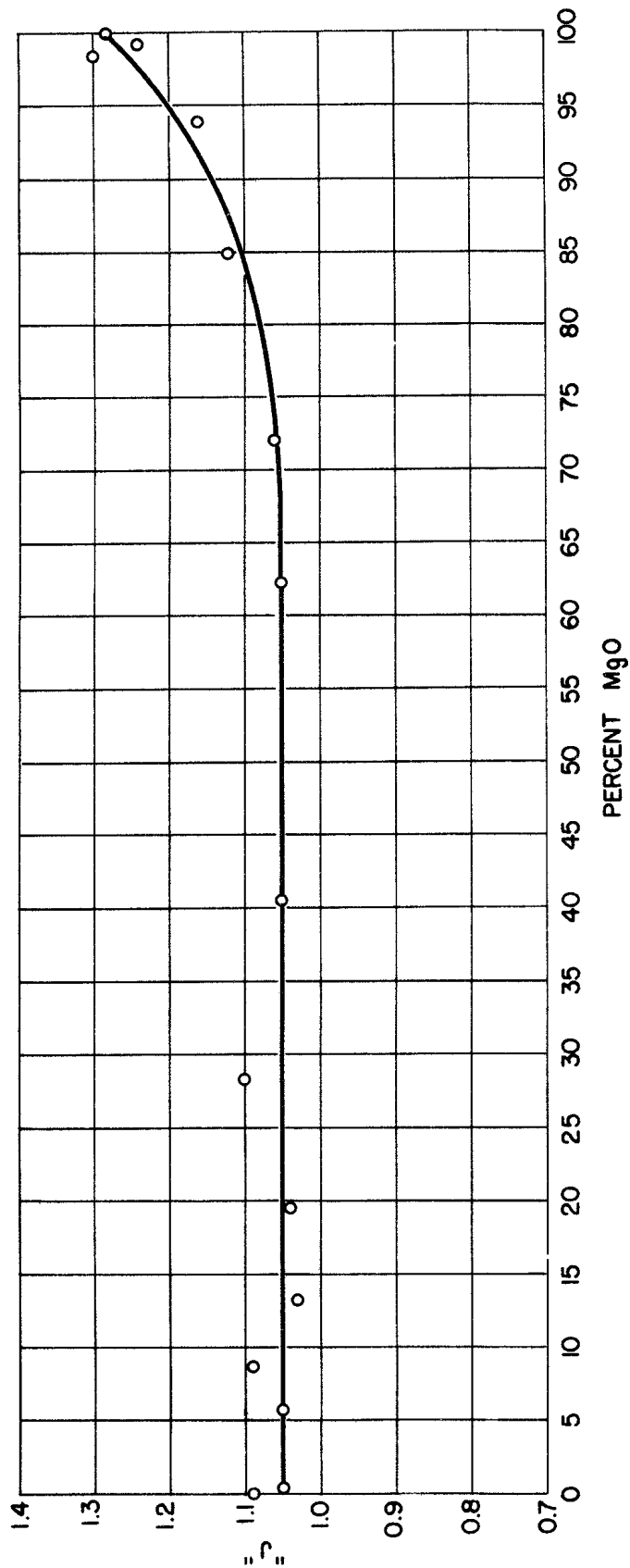


Figure 14. - Effect of the bi-constituent system MgO-SiO<sub>2</sub> upon the intensity of the tin line Sn λ 2840.0 Å.

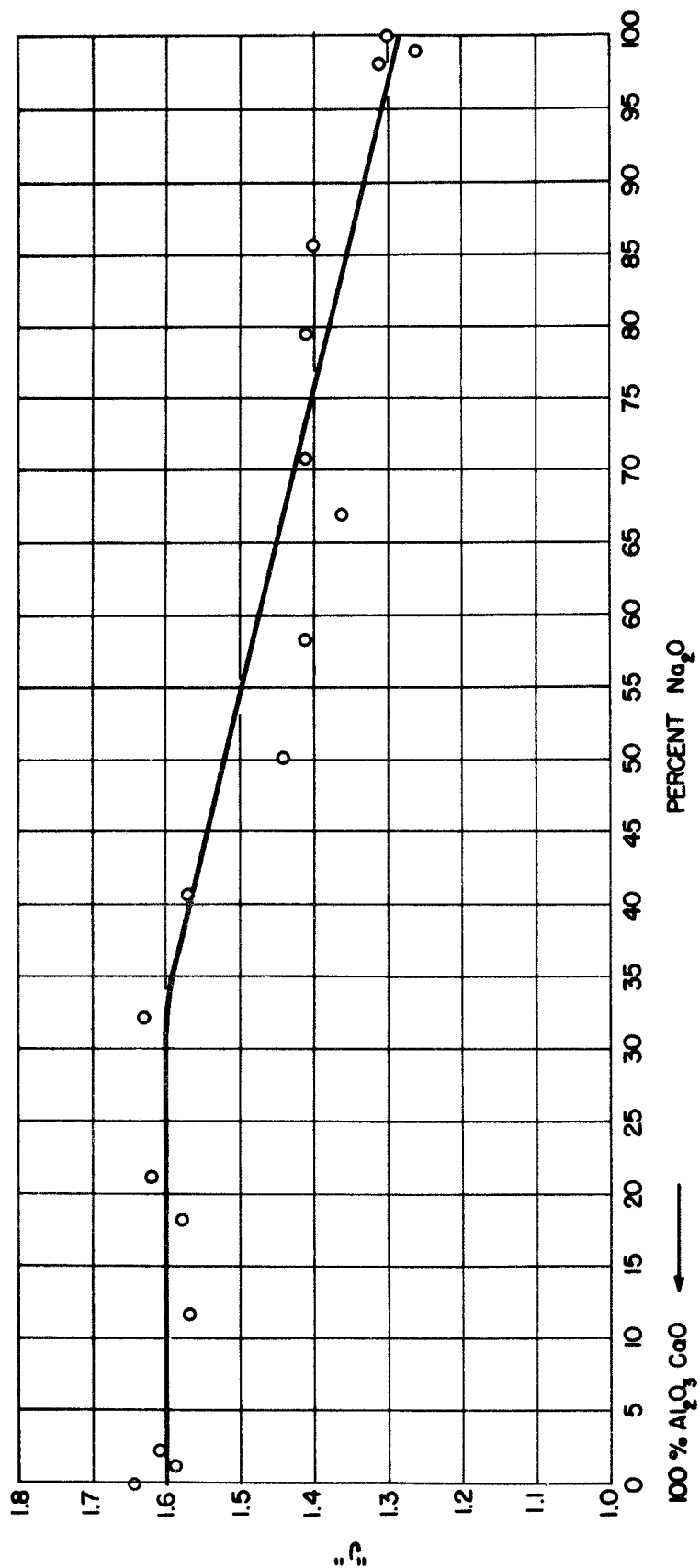


Figure 15. - Effect of the tri-constituent system Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O upon the intensity of the tin line Sn λ2840.0 Å. Al<sub>2</sub>O<sub>3</sub>:CaO in mol proportions of 1:1.

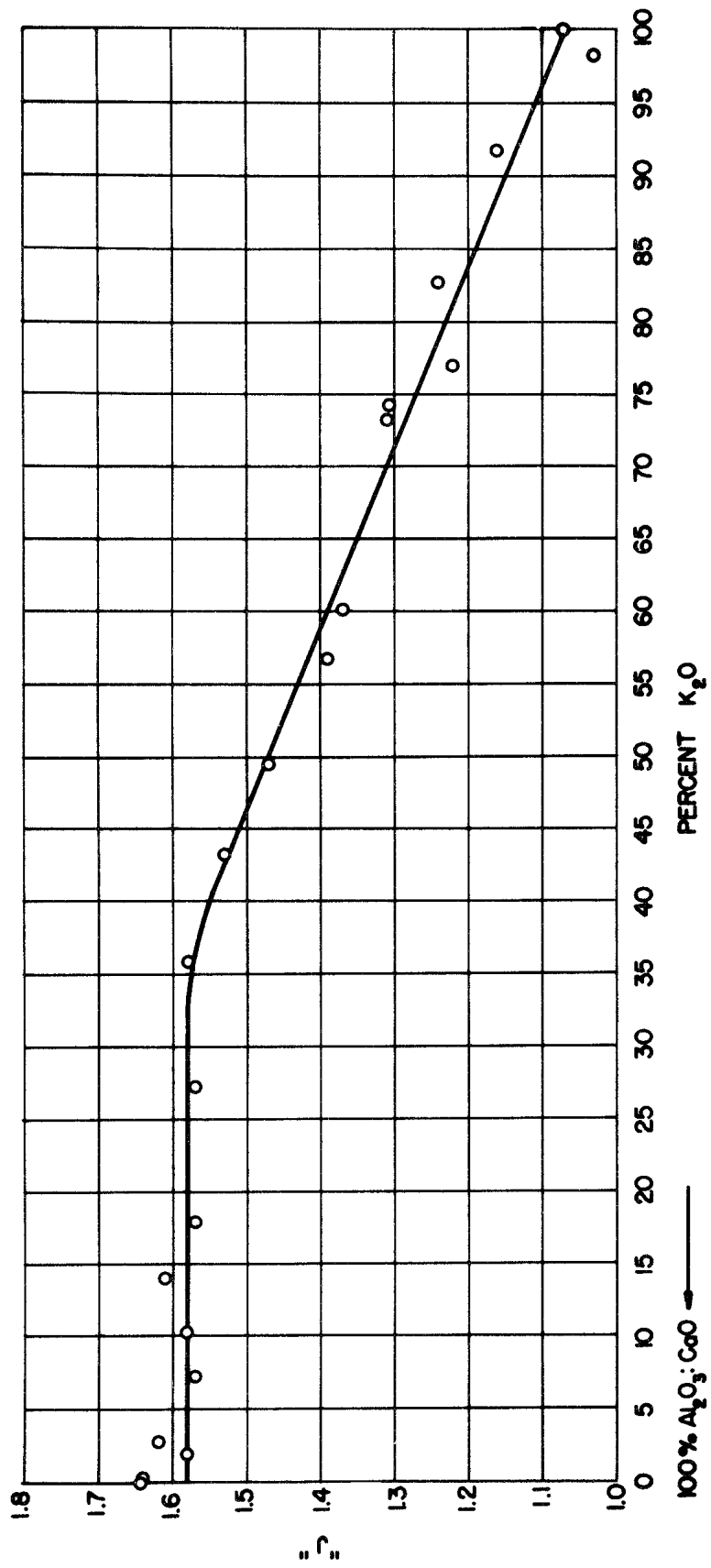


Figure 16. - Effect of the tri-constituent system Al<sub>2</sub>O<sub>3</sub>, CaO, K<sub>2</sub>O upon the intensity of the tin line Sn λ2840.0 Å. Al<sub>2</sub>O<sub>3</sub>:CaO in mol proportions of 1:1.

mixtures were prepared from these primary ones—one containing  $K_2CO_3$  and the other  $Na_2CO_3$ . Percentages of  $K_2O$  and  $Na_2O$  were calculated with respect to  $Al_2O_3$  and  $CaO$ , all other constituents have been ignored. Results are plotted in figures 15 and 16 for the line  $Sn \Lambda 2840.0 \text{ \AA}$ . Beyond about 35 percent  $K_2O$  or  $Na_2O$  there is a marked reduction in line intensity. As  $J$  is proportional to the logarithm of the relative intensity and the curves are roughly linear beyond the 25 percentage points, it is observed that the reduction in line intensity depends approximately exponentially on the percentage  $K_2O$  or  $Na_2O$  present.

After the investigations concerning the effects of bi- and tri-constituent diluents upon the intensity of the tin line  $Sn \Lambda 2840.0 \text{ \AA}$  had been completed, studies were made of mixtures containing the five diluents  $Al_2O_3$ ,  $CaO$ ,  $Fe_2O_3$ ,  $MgO$ , and  $SiO_2$ , as these oxides, either free or combined, compose the gangue of most ores. Mixtures were prepared from the primary mixtures as described; each contained 0.5 percent tin as  $SnO_2$ . The relative percentage of each constituent in each member of this series is given in table 2. Data were obtained with 0.70 milligram samples. Values of  $J$  for the various mixtures, also given in table 2, show that, in general, those mixtures having a high percentage of  $CaO$  plus  $Al_2O_3$  yield higher values of  $J$ , and thus have higher values of line intensity.

Let  $R$  be defined as the ratio

$$[\Sigma \% (Al_2O_3 + CaO) \times 100] / [\Sigma \% (Fe_2O_3 + MgO + SiO_2)];$$

Values for each mixture are given in table 2. In figure 17 is shown a plot of  $J$  versus  $\log_{10} R$ . It is noted that as  $\log_{10} R$  decreases,  $J$  decreases. Although the points are somewhat scattered, the general trend is shown. The conclusion then would seem to be that if enough  $CaO$  and  $Al_2O_3$ , or either, are present, not reduction in line intensity results. To learn whether or not the line intensity could be adjusted to a nearly common value, an equal weight of a  $CaCO_3$ -graphite mixture of known composition and containing no tin was added to a weighed amount of each of the mixtures listed in table 2. After grinding, data again were obtained, 4 milligram samples having been burned in the arc. The relative percentage of each constituent present is shown in table 3. The respective samples are arranged in corresponding order in the two tables. The mean value of  $J$  is 1.98, and deviations therefrom lie within  $\pm 6$  percent, which is no greater than the experimental error. At least, insofar as the oxides listed are concerned, no change in the intensity of the tin line  $Sn \Lambda 2840.0 \text{ \AA}$  results when enough lime is present in the sample.

TABLE 2 Effect of various mixtures upon the relative intensity of the tin line  $Sn \Lambda 2840.0 \text{ \AA}$   
Relative percent of each constituent

$SiO_2$	$Fe_2O_3$	$MgO$	$CaO$	$Al_2O_3$	$R$	$J$
21.6	31.1	12.0	16.2	19.1	54.5	1.51
39.3	22.3	7.4	10.8	20.2	45.0	1.12
45.0	24.3	2.0	18.9	9.8	40.3	1.46
70.3	7.6	1.0	15.1	6.0	26.7	1.40
9.8	62.6	5.0	8.8	13.8	29.2	1.28
15.8	26.8	10.1	41.1	6.2	90.4	1.39
18.2	8.1	51.0	12.4	10.3	29.4	1.12
19.1	10.1	2.1	6.0	62.7	220.0	1.49
34.1	42.1	3.1	2.9	17.8	26.1	1.12
4.1	49.9	3.0	13.0	31.0	78.8	1.50
4.1	60.9	22.8	2.8	9.4	13.9	1.18
4.4	5.8	39.1	45.6	5.1	102.8	1.60
4.6	7.5	28.5	4.0	55.4	146.3	1.62
8.6	4.3	3.1	37.6	46.4	525.0	1.60
60.9	3.1	27.1	5.2	3.7	9.8	1.48
54.3	7.5	3.1	26.6	8.5	54.1	1.51
47.1	7.2	1.9	3.6	40.2	77.9	1.37
54.8	2.3	38.9	3.0	1.0	4.2	1.04
61.8	21.2	5.6	4.7	6.7	12.9	1.12
4.3	5.6	2.3	30.2	27.6	719.7	1.65



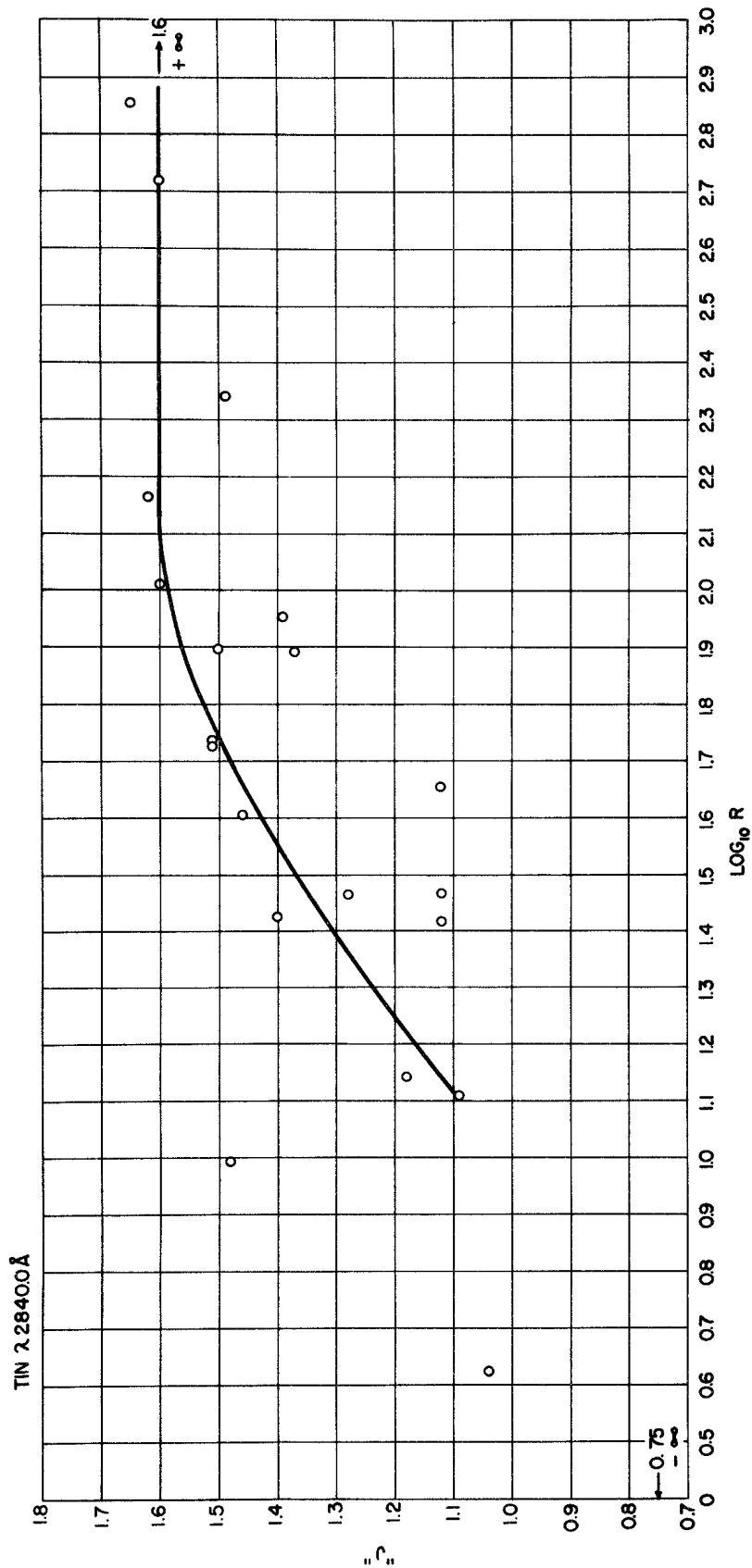


Figure 17. - Effect of mixtures of Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> upon the intensity of the tin line Sn λ 2840.0 Å.

TABLE 3  
Effect of various mixtures, after the addition of lime, upon the relative intensity of the tin line Sn  $\Lambda$  2840.0 Å.

SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	J
13.6	19.6	7.5	47.3	12.0	2.01
23.1	13.1	4.4	47.5	11.9	1.93
26.5	14.3	1.2	52.2	5.8	2.02
41.1	4.4	.6	50.4	3.5	1.94
6.1	39.0	3.1	43.2	8.6	2.00
8.8	14.9	5.6	67.3	3.4	1.98
9.4	4.2	26.4	57.7	5.3	1.95
11.3	6.0	1.3	44.2	37.2	2.00
21.1	26.0	1.9	40.0	11.0	2.08
2.9	34.3	2.1	38.9	21.8	2.08
2.4	36.5	13.6	41.9	5.6	1.98
2.2	2.9	19.7	72.6	2.6	1.96
2.6	4.1	15.8	46.7	30.8	1.90
4.8	2.4	1.7	65.4	25.7	2.02
33.7	1.7	15.0	47.6	2.0	1.96
30.8	4.3	1.8	58.3	4.8	1.91
28.1	4.3	1.1	42.5	24.0	1.90
37.5	1.6	26.6	33.6	.7	2.00
38.2	13.1	3.5	41.1	4.1	1.90
2.3	3.0	1.3	78.7	14.7	1.98
					Mean 1.98

The results of the above investigations show that entstatite, MgSiO<sub>3</sub>, forsterite, Mg<sub>2</sub>SiO<sub>4</sub>, and fayalite, Fe<sub>2</sub>SiO<sub>4</sub>, have the same effects, within the limits of experimental error, upon the intensity of the tin line Sn  $\Lambda$  2840.0 Å as do the corresponding oxides mixed in stoichiometric proportions. It is believed that mixtures of oxides with silica are suitable substitutes for silicates in these investigations. The oxides CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, SiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>, which chemically combined compose in large measure the gangue of ores, having decided effects upon the intensity of the tin line Sn  $\Lambda$  2840.0 Å. The intensity of this line in the presence of a matrix of silica and/or iron oxide is markedly lower than when lime and/or alumina compose the matrix. Silica present in percentages below 50 has little effect upon the intensity of this tin line. When present in greater percentages in the matrix, the effect upon line intensity can be reduced to a minimum by the addition of enough lime so that the percentage of silica in the lime-sample mixture becomes less than 50.

Analysis of ore samples for tin.—To check the results of the previous tests, a number of ore samples from various sources were analyzed for tin. Results are presented in table 4. The tin line employed was Sn  $\Lambda$  2840.0 Å. Each weighed sample was mixed with, roughly, an equal weight of a mixture of CaCO<sub>3</sub>-graphite, the composition of which was in the mol ratio 1:3. The tin also was determined volumetrically by the iodine method.<sup>19</sup> Mean spectrographic results check fairly well with the chemical determinations. The variation in the analyses on any one ore is much greater than desirable. This is to be ascribed primarily to two factors—erratic volatilization in the arc during the burning-off period and non-uniformity of sample. The low weights of samples employed should be noted.

Four of the samples were of a Nevada tin ore. No. 1 was rougher tailings, No. 6 was slimes, and Nos. 7 and 8 were table tailings. The tin was present as cassiterite associated with oxidized iron and with tourmaline. The gangue was a brecciated rhyolite and rhyolite porphyry. An analysis of the head sample showed 62.2 percent SiO<sub>2</sub>, 13.6 percent Fe<sub>2</sub>O<sub>3</sub>, 0.3 percent CaO, 15.0 percent Al<sub>2</sub>O<sub>3</sub>, and 0.15 percent MgO.

Samples 2 and 4 were high in silica, and their analysis with respect to the five oxides discussed was as follows:

<sup>19</sup> Scott, W. W., Standard Methods of Chemical Analysis: D. Van Nostrand and Co., new York, 5<sup>th</sup> ed., vol. 1, 1939.

No.	Al <sub>2</sub> O <sub>3</sub> , %	CaO, %	MgO, %	Fe <sub>2</sub> O <sub>3</sub> , %	SiO <sub>2</sub> , %
2 .....	16.5	2.0	0.50	13.6	60.0
4 .....	15.0	0.3	0.15	13.5	62.2

The total percentage of iron oxide and silica in each of these samples was well over 70. The effects of iron and silicon upon the intensity of the tin line were overcome by the addition of lime.

To be sure that the chemical procedure was accurate, a number of synthetic samples were prepared and submitted to the analyst for analysis, the composition having been unknown to him. Each of these mixtures contained one-third Fe<sub>2</sub>O<sub>3</sub>, one-third MgO, and one-third amphibole by weight, with various percentages of tin as SnO<sub>2</sub>. Results were as follows:

<u>No.</u>	<u>Given: Sn, percent</u>	<u>Found: Sn, percent</u>
1	0.78	0.66
2	0.39	0.38
3	0.17	0.15
4	0.09	0.06

TABLE 4 Spectrographic analyses of ore samples for tin

Sample	Weight of sample, Milligrams	Spectrographic analysis, Percent	Chemical Analysis, Percent
1 .....	2.10	0.19	0.17
	2.16	0.13	
	2.15	0.26	
	2.10	0.16	
	Mean	0.18	
2 .....	0.44	1.00	0.78
	0.58	0.79	
	0.50	0.98	
	Mean	0.92	
3 .....	4.24	0.097	0.08
	4.41	0.088	
	4.35	0.097	
	4.54	0.083	
	Mean	0.091	
4 .....	0.35	1.22	1.10
	0.30	1.28	
	0.33	1.32	
	0.43	0.91	
	Mean	1.18	
5 .....	4.35	0.025	0.07
	4.80	0.026	
	4.68	0.028	
	4.71	0.027	
	Mean	0.027	
6 .....	0.69	0.60	0.49
	0.65	0.64	
	0.67	0.70	
	0.68	0.45	
	Mean	0.60	

TABLE 4 Spectrographic analyses of ore samples for tin (Cont'd)

Sample	Weight of sample, Milligrams	Spectrographic analysis, Percent	Chemical Analysis, Percent
7.	2.21	0.10	0.17
	2.35	0.10	
	2.54	0.14	
	2.22	0.09	
	Mean	0.11	
8 .....	3.60	0.14	0.06
	3.75	0.14	
	Mean	0.14	

LEAD

The lead line we have employed in this work is Pb  $\Lambda$  2853.069 Å, having a relative intensity of 500 R. This line is particularly suitable for use in the analysis of ore samples, as it is one of the persistent lines and interfering elements occur rarely. The effect of the extraneous elements Al, Ca, Mg, Fe, and Si upon the intensity of this line was investigated.

Primary mixtures were prepared in graphite with Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, MgCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. PbO was used as the source of lead, and each mixture contained 0.500 percent of this element. The graphite concentrations in these mixtures were the same as those used in the investigations concerning tin.

To learn whether or not the five elements of these mixtures would have the same effect upon line intensity as in the case of tin, 4.00-milligram samples of each were burned in the arc and spectrograms were taken. Mean optical densities are given in table 5. It is to be noted that the order in reduction in line intensity is the same as with tin.

TABLE 5 Effect of a number of oxides upon the relative intensity of the lead line Pb  $\Lambda$  2853.069 Å

	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Optical density D	1.65	1.65	1.50	0.80	0.75

In figure 18 is shown an optical density D versus the logarithm of the weight of lead in gamma curve. The base material was Al<sub>2</sub>O<sub>3</sub> in one instance and CaCO<sub>3</sub> in the other; both materials, within the limits of experimental error, had the same influence on the intensity of this particular lead line.

As in the case of tin, investigations were made concerning the tri-constituent system Al<sub>2</sub>O<sub>3</sub>, CaO, and SiO<sub>2</sub>. Each sample that was volatilized in the arc weighed 3.00 milligrams and contained 15 gamma of lead as PbO. Results are presented in figure 19. The diagram is similar to that for tin (fig. 13). At a concentration of about 50 percent silica, a marked decrease in line intensity commences and continues to 100 percent silica. This occurs for lime-silica, alumina-silica, or mixtures of all three constituents. Below 50 percent silica, no marked differences in line intensity occur.

Fairly complete investigations were made concerning the effects of penta-constituent diluents upon the intensity of the aforementioned lead line. The experimental procedure was the same as that made in the investigations concerning tin. 3.00-milligram samples were burned in the arc. Data concerning the relative composition of these mixtures are shown in table 6. In figure 20 are plotted values of  $\int$  versus log<sub>10</sub> R, R having been defined previously. The decrease in intensity with increase in  $\Sigma$  (MgO + Fe<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub>) is roughly linear. After the addition of an equal weight of a CaCO<sub>3</sub>-graphite mixture containing no lead to a weighed amount of each mixture of the series, they were again ground mechanically. 4.00-milligram samples were burned in the arc, and spectrograms were taken. Results are given in table 7, and values of  $\int$  versus log<sub>10</sub> R are plotted in figure 21. The points are somewhat more scattered than in the case of tin, but this, in part at least, is due to experimental error.

We conclude that, in general, if the sum of the percentages of alumina and lime is about 50 percent or more in samples containing the aforementioned oxides, then the intensity of the lead line Pb  $\Lambda$  2833.1 Å is approximately constant for such mixtures.

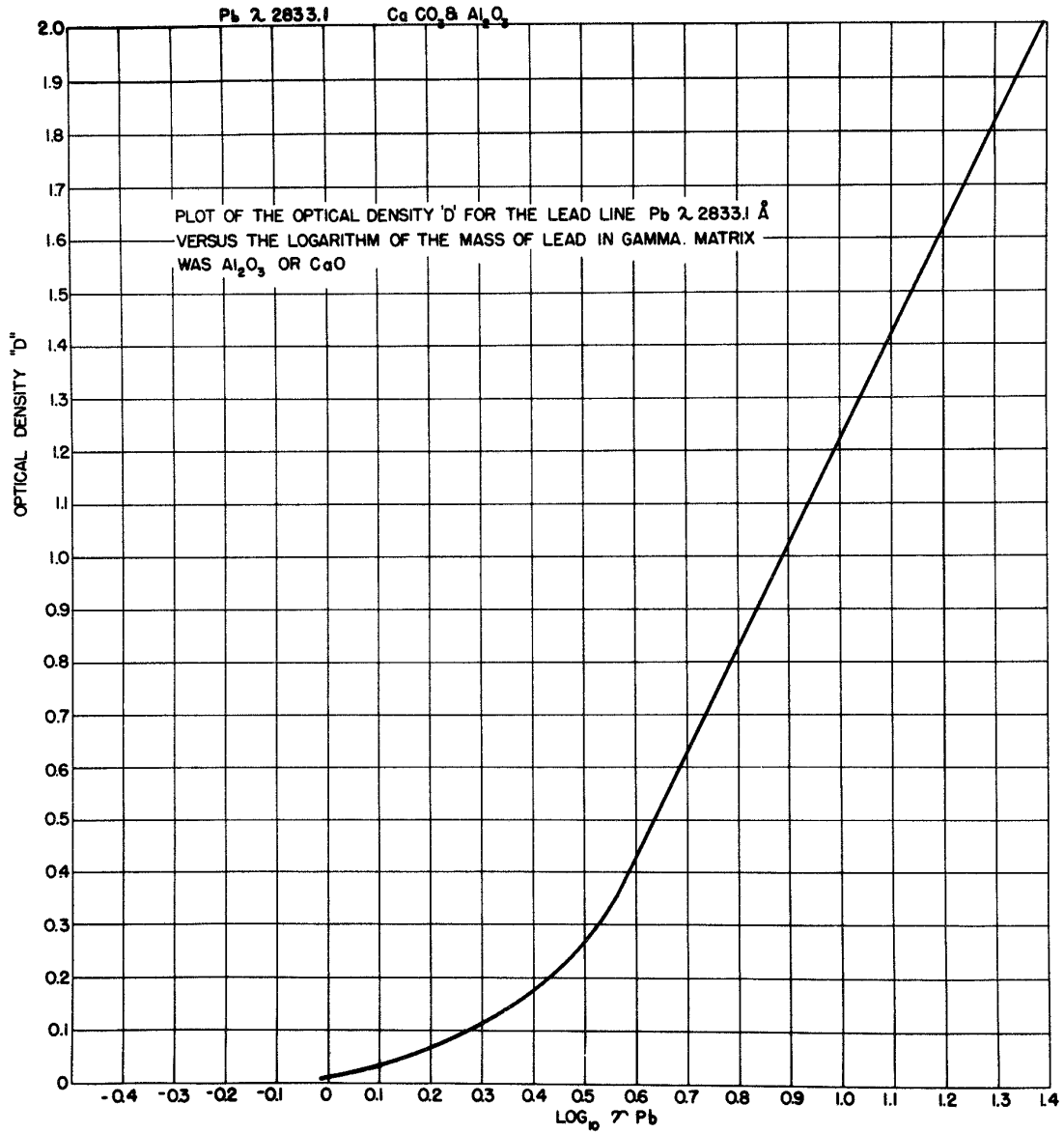


Figure 18. - Plot of the optical density D for the lead line Pb  $\lambda$ 2833.1 Å versus the logarithm of the mass of lead in gamma. The matrix was Al<sub>2</sub>O<sub>3</sub> or CaO.

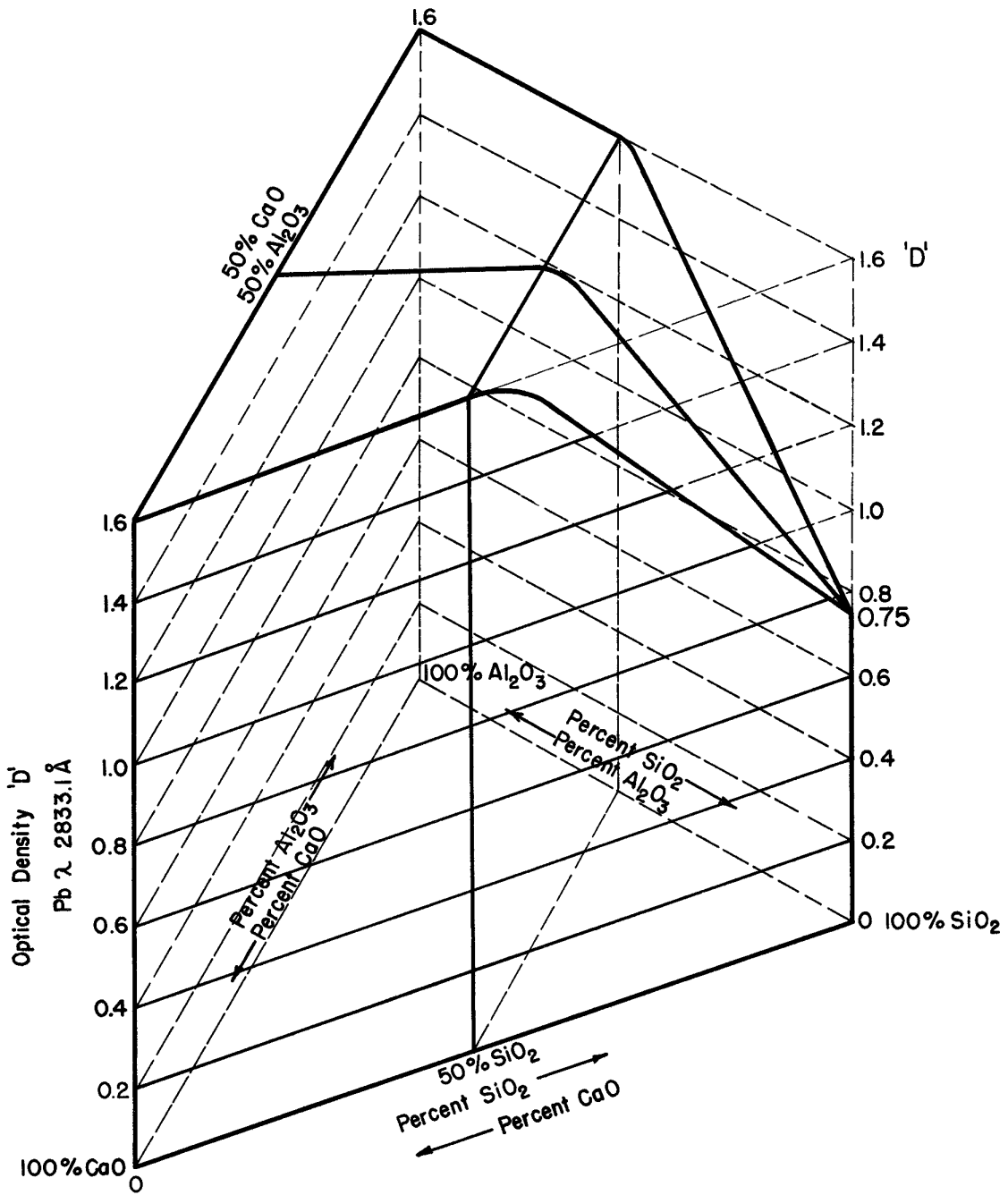


Figure 19. - Triangular space diagram showing the effect of CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and mixtures thereof upon the optical density of the lead line Pb λ 2833.1 Å.

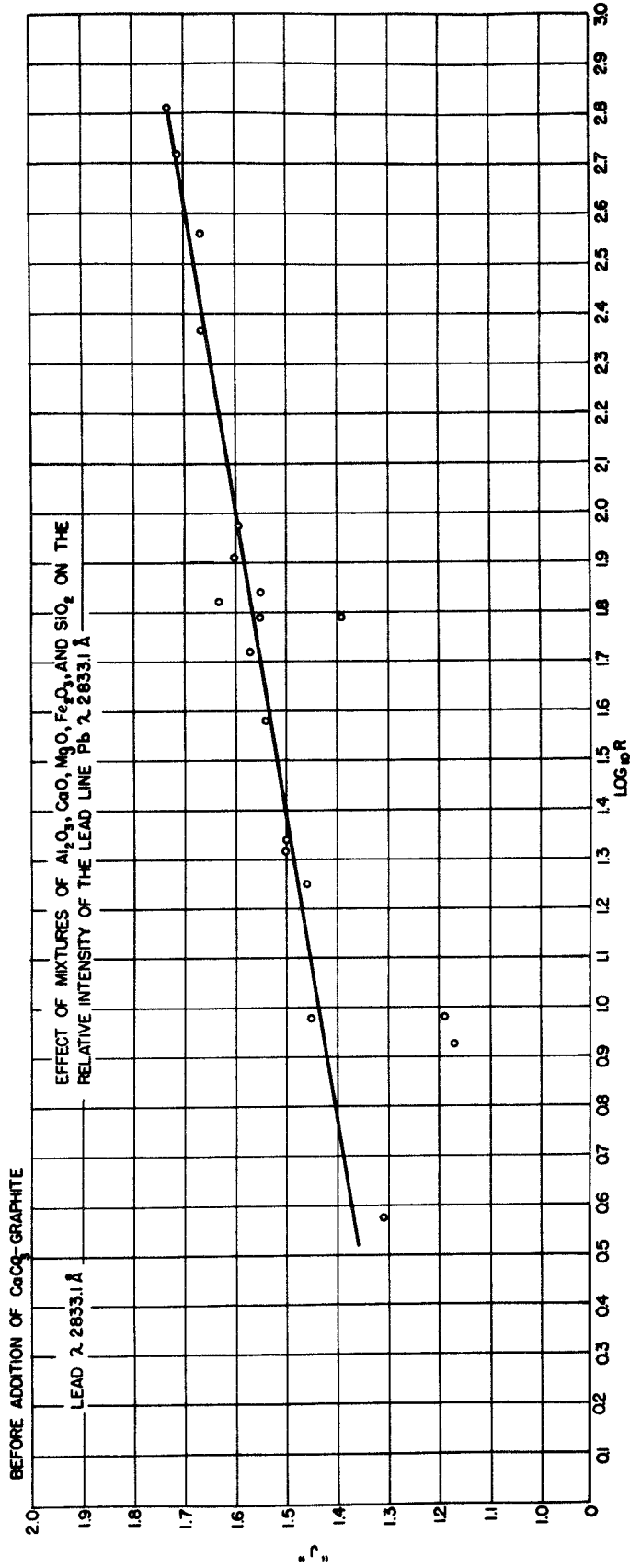


Figure 20. - Effect of mixtures of Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> upon the intensity of the lead line Pb λ 2833.1 Å.

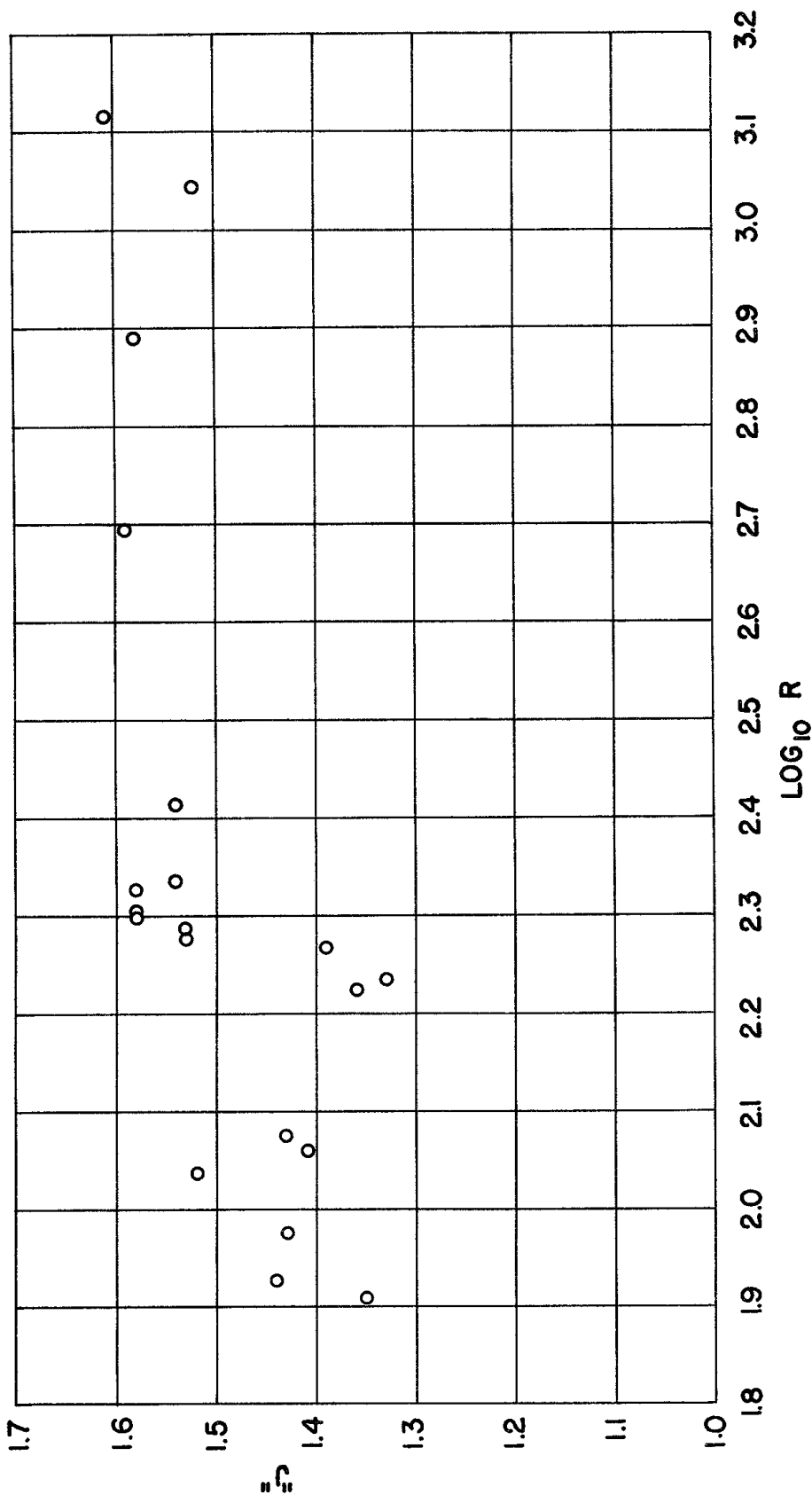


Figure 21. - Effect of mixtures of Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, Fe<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> after further addition of lime upon the intensity of the lead line Pb λ 2833.1 Å.



TABLE 6 Effect of various mixtures upon the intensity of the lead line Pb  $\Lambda$  2833.1 Å  
Relative percentage of each constituent

SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	R	J
48.0	46.8	1.5	1.9	1.8	3.8	1.31
20.2	29.4	12.1	17.5	20.8	62.1	1.39
6.4	4.8	2.3	34.0	52.5	641.8	1.73
4.2	15.1	2.5	53.8	24.4	360.2	1.66
50.5	9.8	1.4	16.5	21.8	62.1	1.55
10.5	67.3	5.0	13.6	3.6	20.6	1.50
3.6	24.2	44.6	15.8	11.7	38.0	1.54
5.3	6.9	4.0	63.6	20.2	517.3	1.71
1.1	23.7	5.8	7.5	61.9	226.2	1.66
52.8	36.7	1.8	5.9	2.8	9.5	1.19
60.0	7.8	23.5	4.6	4.1	9.5	1.45
59.5	3.9	2.1	32.5	2.0	52.7	1.57
51.8	5.2	2.2	4.0	36.8	69.1	1.55
29.1	62.2	0.9	3.3	4.5	8.5	1.17
2.4	10.7	68.9	9.5	8.5	22.0	1.50
7.2	16.2	55.3	9.5	11.8	27.1	1.36
2.1	51.5	1.3	7.9	37.2	81.9	1.60
3.9	54.9	1.7	35.7	3.8	65.4	1.63
4.3	57.3	23.2	12.0	3.2	17.9	1.46
26.4	21.0	4.0	22.1	26.5	94.7	1.59

TABLE 7 Effect of various mixtures, after the addition of lime, upon the relative intensity of the lead line Pb  $\Lambda$  2833.1 Å after the addition of—

SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	R	J
27.5	26.9	0.9	43.7	1.0	80.8	1.35
10.8	15.7	6.5	35.9	11.1	202.7	1.58
3.4	2.5	1.2	65.2	27.7	1304.5	1.61
2.2	7.9	1.3	75.8	12.8	775.7	1.58
27.3	5.3	0.7	54.9	11.8	199.9	1.58
6.1	38.9	2.9	50.1	2.0	109.0	1.52
1.8	11.7	21.6	59.2	5.7	184.8	1.39
2.7	3.6	2.0	81.3	10.4	1100.5	1.52
0.6	13.0	3.2	49.3	33.9	494.9	1.59
29.8	20.7	1.0	46.9	1.6	94.3	1.43
30.5	4.0	12.0	51.4	2.1	115.1	1.41
31.4	2.1	1.1	64.4	1.0	189.4	1.53
28.1	2.8	1.2	48.0	19.9	211.9	1.58
17.0	36.5	0.6	43.3	2.6	85.0	1.44
1.1	4.9	31.2	58.9	3.9	168.7	1.36
3.4	7.6	25.9	57.6	5.5	171.2	1.33
1.2	29.7	0.8	46.9	21.4	215.8	1.54
2.2	30.9	1.0	63.8	2.1	194.1	1.53
2.3	30.8	12.5	52.7	1.7	119.2	1.43
14.3	11.3	2.2	57.8	14.4	259.6	1.54

Analysis of ore samples for lead. A number of ore samples were analyzed for lead. The procedure was the same as that used in the analyses for tin. Approximately an equal weight of a CaCO<sub>3</sub>-graphite mixture was mixed with each weighed sample prior to burning in the arc. The standard analytical curve employed was that of figure 18. Results of the analyses are presented in table 8. The analyses on any one ore deviate considerably from the mean, but mean values approximate chemical analyses. For

samples containing 1 percent lead or less, an electrolytic method<sup>20</sup> was used, whereas for greater concentrations the ordinary molybdate method was employed.

TABLE 8 Spectrochemical analyses of ore samples for lead

Sample and description	Weight of sample, milligrams	Spectrographic analysis, percent	Chemical analysis, percent
1			
Source unknown	1.94	0.35	
	1.78	0.42	
	1.80	0.40	
		Mean 0.39	0.40
2			
Source Unknown	2.90	0.53	
	1.86	0.68	
	1.73	0.65	
	1.71	0.63	
		Mean 0.62	0.36
3			
Slime	1.65	0.40	
16.3% Fe, 23.3% Mn,	2.05	0.29	
24.8% SiO <sub>2</sub>	2.09	0.28	
		Mean 0.32	0.36
4			
Zinc concentrate.	1.94	0.41	
32.8% Zn, 8.0% Fe.	1.72	0.48	
Highly siliceous,	1.92	0.48	
sphalerite, galena			
Nevada		Mean 0.46	0.56
5			
Zinc concentrate.	1.92	0.30	
54.8% Zn, 7.0% Fe.	1.97	0.23	
As in No. 4, but a	1.94	0.36	
somewhat different	1.38	0.41	
sample. Nevada		Mean 0.32	0.34
6			
Tailings. 1% Fe, 2.6%	2.00	0.22	
Zn. Sphalerite and	1.66	0.35	
galena disseminated	3.18	0.26	
through quartz and	4.00	0.29	
calcite. High in silica.	3.70	0.24	
Washington	5.18	0.30	
		Mean 0.28	0.24
7			
Zinc concentrate.	1.97	0.42	
48.0% Zn, 7.5% Fe.	1.70	0.76	
Galena, sphalerite,	2.24	0.55	
arsenopyrite, and pyrite.	2.61	0.31	
Washington		Mean 0.51	0.65
8			
Composite tailings.	3.50	0.30	
Idaho	3.39	0.35	
	3.98	0.28	
		Mean 0.31	0.14

<sup>20</sup> Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists: Fifth ed., 1940, p. 400. Published by the association, Washington, D. C.

TABLE 8 Spectrochemical analyses of ore samples for lead (Cont'd)

Sample and description	Weight of sample, milligrams	Spectrographic analysis, percent	Chemical analysis, percent
9			
Zinc concentrate	2.82	1.99	
46.6% Zn, 11.9% Fe.	3.01	2.12	
Sphalerite, galena, pyrite, magnetite associated with quartz and calcite. Colorado	2.98	2.32	
		Mean 2.14	2.2
10			
Table concentrate.	2.94	4.01	
Cerrussite, malachite, azurite, calamine, mixite, pyrite in a gangue of silica and clay. Utah	2.70	3.84	
	3.00	3.45	
	2.70	4.32	
		Mean 3.90	3.7
11			
Cleaner tailings.	2.91	1.17	
3.6% MoS <sub>2</sub> , 84.2% acid insoluble. Primarily a quartz porphyry inclusions of molybdenite, pyrite, galena, and chalcopyrite. Montana	2.90	1.03	
	2.92	1.26	
	2.95	1.11	
		Mean 1.14	1.0
12			
Rougher tailings.	2.98	1.57	
32.4% Fe. Sphalerite, chalcopyrite, pyrite, galena, hematite and manganese oxide scattered throughout a gangue of quartz and altered feldspars. Colorado	2.98	1.87	
	2.94	1.53	
		Mean 1.66	1.5
13			
Rougher tailings.	3.00	2.14	
34.6% Fe, 14.6% acid insoluble. Galena, sphalerite, pyrite, magnetite, scattered through quartz and calcite. Colorado	2.82	2.01	
	2.92	1.94	
	2.95	2.22	
		Mean 2.08	2.0
14			
Iron concentrate.	2.76	0.76	
10.2% Ag, 4.6% Zn. Washington	2.87	0.63	
	2.78	0.54	
	2.89	0.92	
		Mean 0.71	0.6

GERMANIUM

Germanium is found in some sulfide ores and particularly in zinc blends. It also has been reported to occur in many complex silicates.<sup>21</sup> Perhaps the most significant source of the element is germanite, a mineral from Southwest Africa, some samples of which have been reported to contain as much as 8.7 percent.<sup>22</sup> In general, however, it is found in concentrations considerably below a few tenths of 1 percent.

The most sensitive neutral atom line of germanium lies outside the region 2,000-10,000 Å; the second sensitive line is Ge  $\Lambda$  3039.064 Å and has an intensity of 1,000.<sup>23</sup> It is suitable for use in ore analysis. Possible interfering lines of importance are In I  $\Lambda$  3039.356 Å and Fe  $\Lambda$  3039.316 Å. However, the Baird spectrograph has sufficient dispersion and resolution to prevent masking by these lines.

Preparation of GeO<sub>2</sub>. Germanium metal is unsuitable for use in the preparation of standards by the total-energy method, as it is rather brittle and would be difficult to disperse readily. We have used the oxide, which was prepared in the following way:

Pure metallic germanium was pulverized to minus 20-mesh in a diamond mortar. It was then placed in a flask connected with a Liebig condenser and aqua regia was added. The metal is rapidly converted to the tetrachloride if first pulverized. As GeCl<sub>4</sub> is a liquid having a vapor pressure (b.p. 86° C.) comparable to that of water, the condenser served to prevent any great loss. After the metal had completely dissolved, the GeCl<sub>4</sub> was distilled off and collected in distilled water. Ammonia was added to this solution until it was just basic to litmus. The precipitate was filtered off, washed five times with dilute ammonia (1:10), dried at 100° C., and finally ignited at 700° C. for 30 minutes. Yield: 74 percent of theoretical from ½ gram sample of metal. Traces of Fe, Si, and Mg were found to be spectrographically present in this product.

#### Effect of extraneous elements on line intensity

In view of the fact that germanium often is found in zinc blends, which frequently contain a high percentage of iron pyrite, a study was made of the bi-constituent system FeS<sub>2</sub> and ZnS. The ZnS employed was the ordinary chemically pure grade of commerce, whereas the source of FeS<sub>2</sub> was a sample of iron pyrites good quality. Hand-picked pyrite was ground to about 65-mesh, conditioned with NaCN and CaO, and the copper sulfide removed by floatation with xanthate and pine oil. Analysis of the pyrite tailings showed 45.0 percent Fe (theoretical for FeS<sub>2</sub>, 46.54 percent), 52.0 percent S (theoretical 53.46 percent), 0.10 percent SiO<sub>2</sub>, and 0.30 percent acid insoluble matter. Primary mixtures containing graphite in a 2:1 ratio and 0.15 percent GeO<sub>2</sub> were prepared for the two sulfides. Three mixtures were prepared from the two primary ones, the relative percentage of ZnS in each being given in table 9. These percentages are based upon ZnS and FeS<sub>2</sub>, the graphite and GeO<sub>2</sub> having been ignored. 3.00-milligram samples were burned in the arc. Within the limits of experimental error, mean values for  $\int$  for the five mixtures are the same. No differences in intensity of the aforementioned germanium line were noted.

TABLE 9                      Effect upon the intensity of the germanium line Ge  $\Lambda$  3039.1 Å  
by mixtures of FeS<sub>2</sub>, ZnS, and graphite

Relative percentage of ZnS	$\int$
0	1.50
25.1	1.47
49.9	1.47
74.6	1.51
100.0	1.54

An optical density versus log  $\gamma$  curve employing the germanium line Ge  $\Lambda$  3039.1 Å is shown in figure 22. The base materials were Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, and ZnS, respectively, and within the limits of experimental error the same standard curve was obtained for each mixture.

As in the case of tin and lead, the bi- and tri-constituent systems made up of Al<sub>2</sub>O<sub>3</sub>, CaO, and SiO<sub>2</sub> were investigated. 3.00-milligram samples were volatilized in the arc. Results are shown diagrammatically

<sup>21</sup> Papish, J., *Economic Geology*, vol. 23, 1928 p. 660; *ibid.*, vol. 24, 1929, p. 470.

<sup>22</sup> Hopkins, B. S., *loc. cit.*

<sup>23</sup> Harrison, G. R., *loc. cit.*

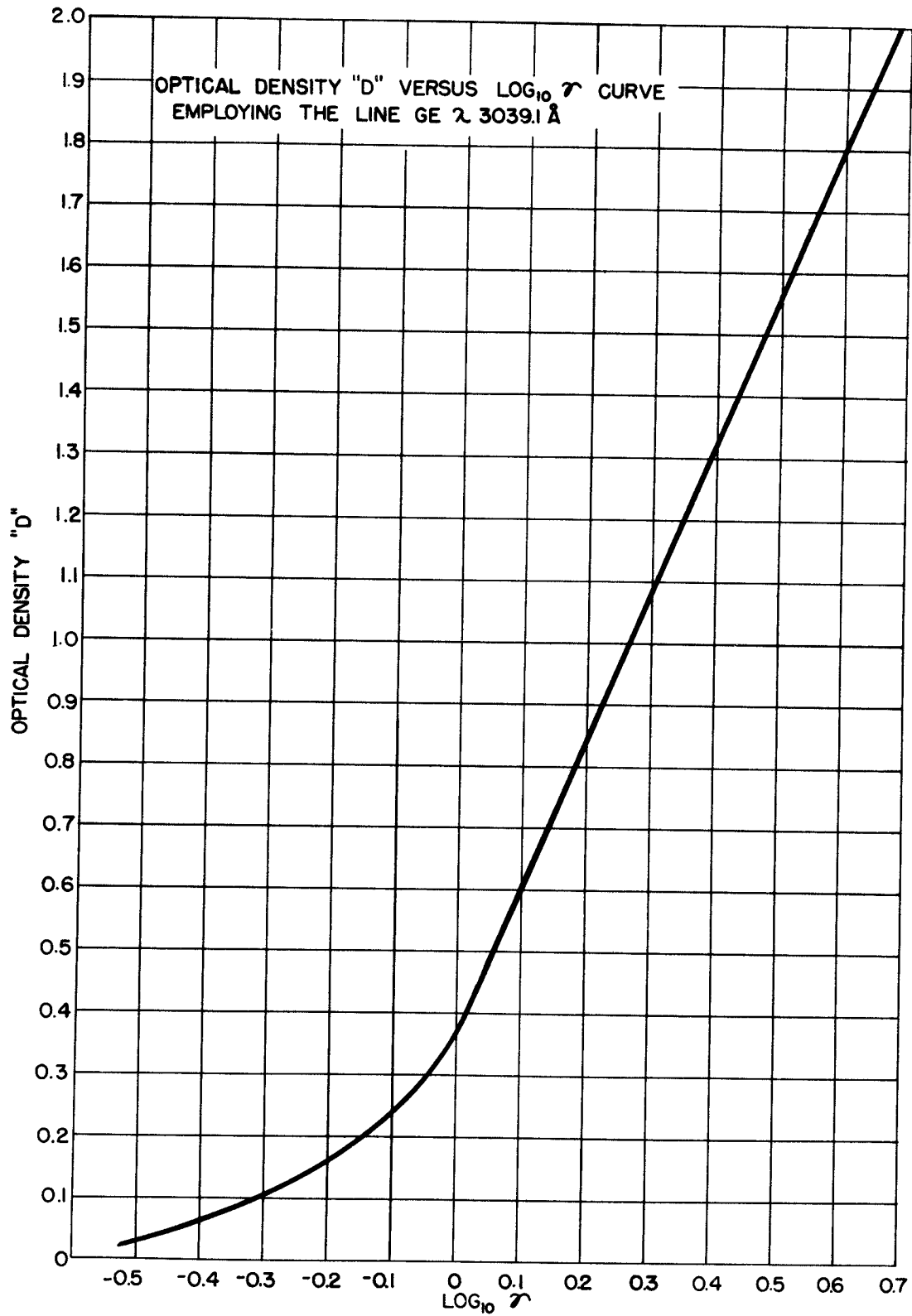


Figure 22. - Optical density,  $D$ , versus  $\log_{10} \tau$  curve employing the line Ge  $\lambda$  3039.1 Å.

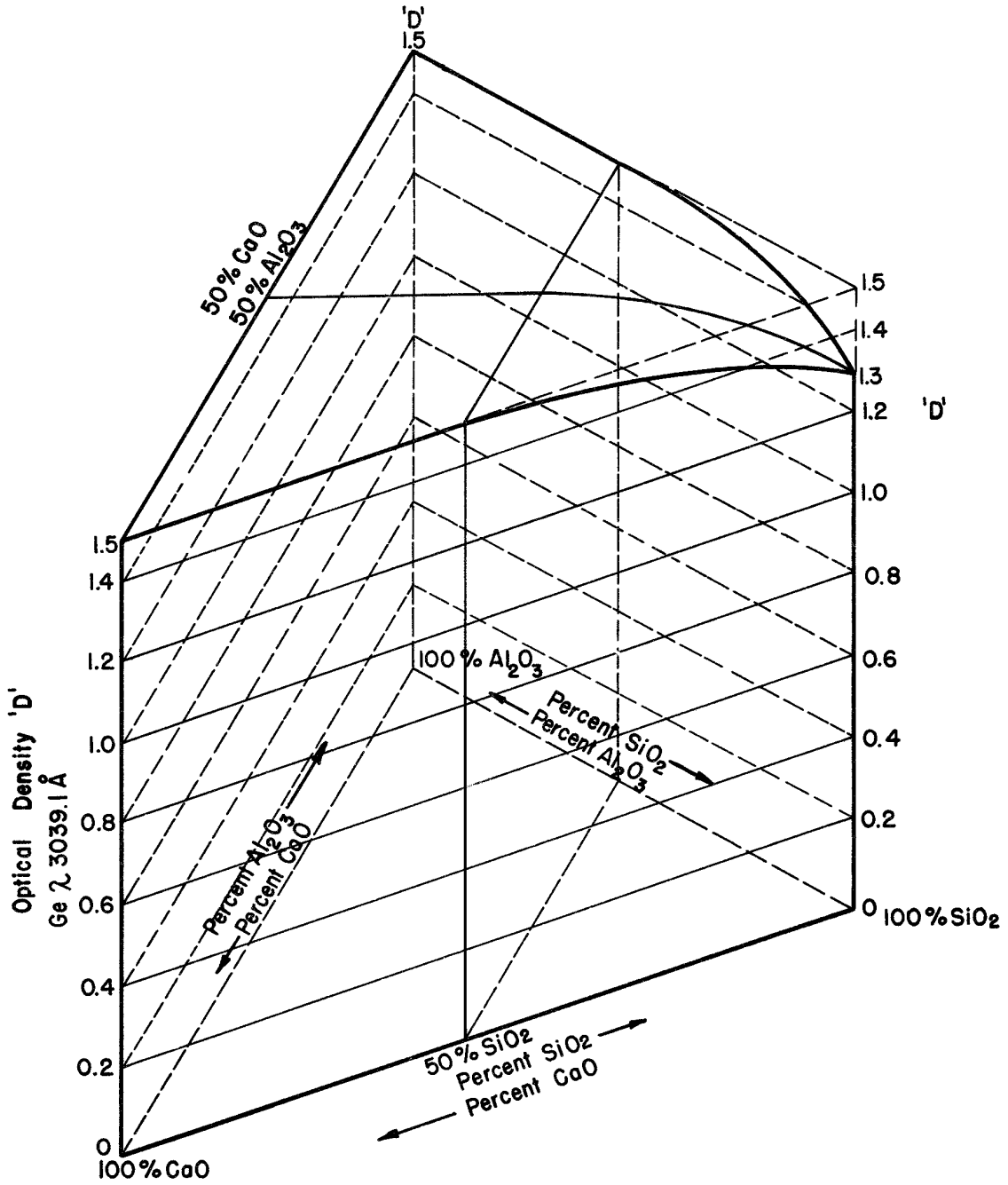


Figure 23. - Triangular space diagram showing the effect of CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and mixtures thereof upon the optical density of Ge λ3039.1 Å.

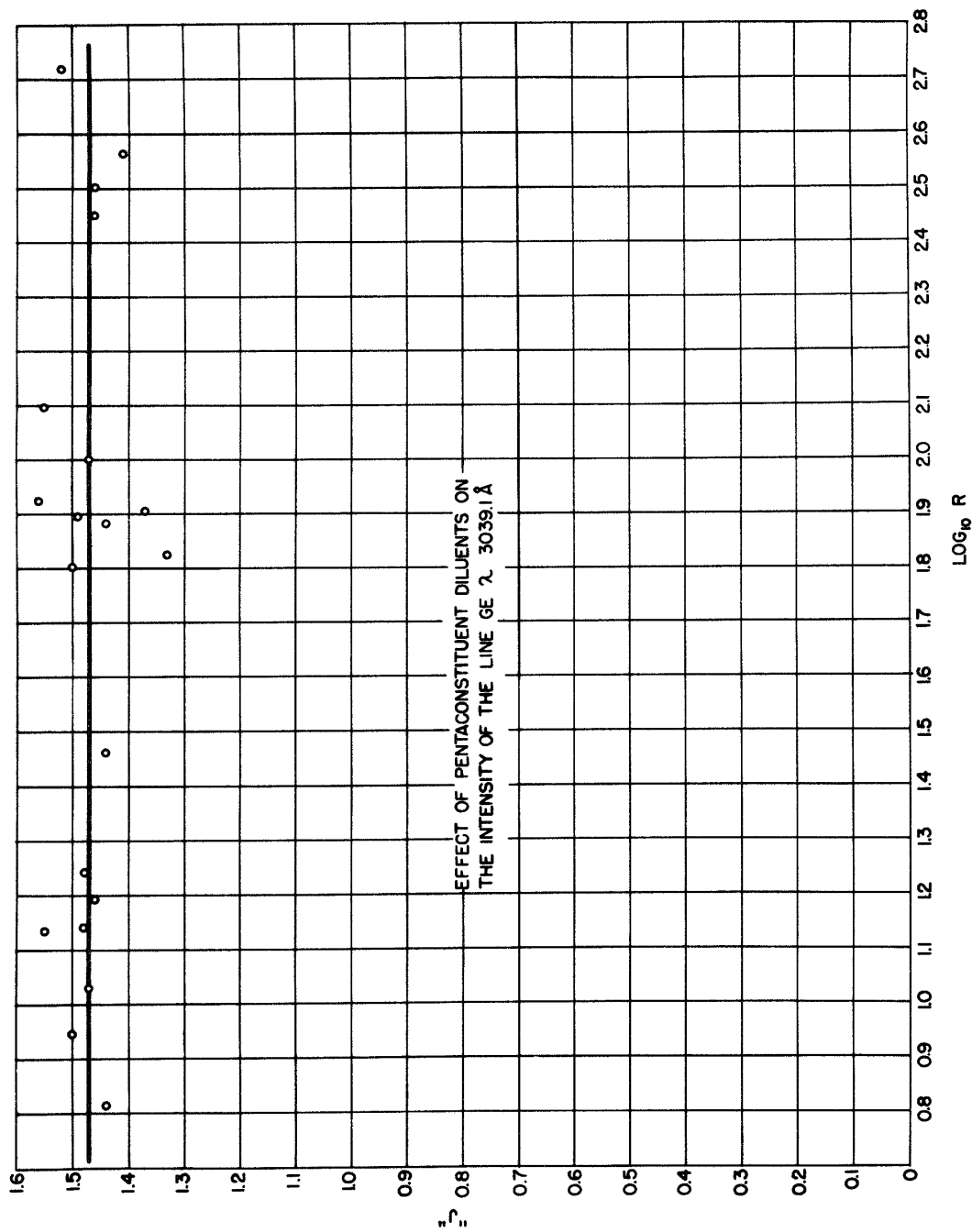


Figure 24. - Effect of penta-constituent diluents upon the intensity of the line Ge  $\lambda$  3039.1 Å.

in figure 23. The reduction in line intensity with increase in SiO<sub>2</sub> concentrations was much less than in the case of tin.

Primary mixtures, each of which contained 0.15 percent GeO<sub>2</sub>, were prepared in Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, MgCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. These primary mixtures contained the same mol fractions of graphite as those used in the work concerning tin and lead. To determine whether or not these mixtures would have the same effect on line intensity as in the case of tin and lead, 3.00-milligram samples were volatilized in the arc, and spectrograms were taken. Mean optical densities are presented in table 10. The order of reduction of line intensity is the same as for tin and lead, but less marked.

TABLE 10  
Effect of a number of oxides upon the relative intensity  
of the germanium line Ge  $\Lambda$  3039.1 Å

	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
Optical density D	1.8	1.8	1.6	1.5	1.5

Penta-constituent mixtures were prepared from the described primary mixtures. 3.00-milligram samples were burned in the arc. Results are presented in table 11. It is to be observed that there were not the marked differences that were obtained with tin. Values of  $J$  are plotted versus log<sub>10</sub> R in figure 24. Nearly all of them lie between  $J = 1.4$  and 1.5.

TABLE 11  
Effect of various mixtures upon the relative intensity of the  
germanium line Ge  $\Lambda$  3039.1 Å

SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	R	$J$
78.8	8.4	3.1	3.3	6.4	10.7	1.47
3.9	87.8	2.2	2.4	3.7	6.6	1.44
7.9	14.3	65.8	3.9	8.1	13.6	1.55
8.2	9.8	3.3	70.5	8.2	367.1	1.41
6.0	7.1	2.9	3.2	80.8	523.8	1.52
36.9	51.9	3.1	3.6	4.5	8.9	1.50
46.3	10.2	28.6	4.4	10.5	17.5	1.48
46.5	10.5	4.2	30.7	8.1	63.5	1.50
40.6	9.9	3.9	4.6	41.0	84.0	1.56
18.7	19.7	17.0	25.3	19.3	80.7	1.37
4.7	52.5	29.3	8.8	4.7	15.7	1.46
7.7	48.8	3.3	34.3	5.9	67.1	1.33
21.9	31.9	2.1	1.8	42.3	79.1	1.49
14.0	14.4	28.3	33.0	10.3	76.3	1.44
12.3	11.2	20.8	6.1	49.6	125.6	1.55
9.0	10.3	4.4	32.9	43.4	321.2	1.46
42.3	30.4	4.8	7.1	15.4	29.0	1.44
30.0	56.0	1.8	6.7	5.5	13.9	1.48
6.3	16.8	3.0	35.6	38.3	282.3	1.46
22.2	19.0	8.7	26.9	23.2	100.4	1.47

Analysis of ore samples for germanium. The results of the previous work indicate that it is not necessary to add a spectrographic buffer in making an analysis for germanium, particularly in a zinc blend, provided the line Ge  $\Lambda$  3039.1 Å is used. No investigations were made concerning other germanium lines.

A number of ore and mineral samples, including complex silicates, were examined spectrographically in a search for this element. It was found present in the four ores listed in table 12. No buffer was added for the analysis of these ores. Preliminary spectrographic examination of the germanite from Southwest Africa showed the germanium content to be so high that it could not be readily analyzed when using the standard without dilution. The Ge  $\Lambda$  3039.1 Å line was too dense, even when samples of very low weight were employed, for accurate densitometer measurements to be made. Consequently, a mixture of 12 percent by weight of this ore with a CaCO<sub>3</sub>-graphite mixture was prepared and analyzed.



Chemical analyses for germanium in the two zinc ores were made by the method of Hybbinette and Sandell.<sup>24</sup>

TABLE 12 Analysis of ore samples for germanium

Sample	Sample weight, Milligrams	Spectrographic analysis, Percent	Chemical analysis, Percent
Enargite, Butte, Mont.	2.28	0.038	
	2.21	0.039	
	2.19	0.035	
	2.50	0.037	
	Mean	0.037	
Zinc ore No. 1, Nevada	2.48	0.020	0.025
	2.55	0.023	
	2.59	0.026	
	3.80	0.023	
	Mean	0.023	
Zinc ore No. 2, Nevada	2.93	0.011	0.009
	2.93	0.015	
	2.67	0.013	
	1.65	0.017	
	Mean	0.014	
Germanite with tennantite, Southwest Africa		3.970	
		4.130	
		Mean 4.050	

### CONCLUSIONS

Results for germanium, tin, and lead indicate that after further research and development, the total-energy method of spectrochemical analysis will be quite suitable for the general analysis of ore samples.

Investigations were made of the effects of various extraneous materials, particularly the oxides  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ , which enter into the formation of complex silicates, upon the intensities of the tin line  $\text{Sn } \Lambda 2840.0 \text{ \AA}$ , of the lead line  $\text{Pb } \Lambda 2833.1 \text{ \AA}$ , and of the germanium line  $\text{Ge } \Lambda 3039.1 \text{ \AA}$ .

Enstatite, forsterite, and fayalite have the same effects, within the limits of experimental error upon the intensity of the tin line as do the corresponding mixtures of the oxides in stoichiometric proportions. It is believed that mixtures of oxides with silica are suitable substitutes for silicates in such investigations. The intensities of  $\text{Sn } \Lambda 2840.0 \text{ \AA}$  and  $\text{Pb } \Lambda 2833.1 \text{ \AA}$  are highest when a matrix of  $\text{Al}_2\text{O}_3$  or  $\text{CaCO}_3$  is employed, there being no observed difference in the effects of these two compounds. The intensities are progressively decreased  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SiO}_2$ , and graphite, respectively.

The effects upon these lines of bi-constituent and tri-constituent mixtures prepared from  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and  $\text{SiO}_2$  were investigated. When present in such mixtures in percentages greater than 50 percent, silica markedly reduces the intensities of the tin and lead lines, but the reduction in intensity for the germanium line is much less.

The effects upon line intensities of penta-constituent diluents containing various percentages of the five listed oxides were studied also. Again it was found that high percentages of silica and iron markedly reduced the line intensities of tin and lead. By the addition of enough lime to mixtures high in silica and/or iron, the reduction in line intensities is kept to a minimum. In the case of germanium, similar studies were made, but the effects upon line intensity were not significant.

A number of ore samples were analyzed spectrographically for tin or lead after a lime-graphite mixture had been added to the samples. It was not deemed necessary to add lime prior to analysis to

<sup>24</sup> Hybbinette, A., and Sandell, E. B.: Jour. Ind. and Eng. Chem., anal. ed., vol. 14, 1942, p. 715.

samples containing germanium. Analytical results for these elements compared favorably with those obtained by chemical methods.