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SPARK SPECTROGRAPHIC ANALYSIS OF COMMERCIAL TIN[1]

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ABSTRACT

A procedure is described in detail for the simultaneous spectrographic determination of antimony, arsenic, bismuth, cadmium, copper, indium, iron, lead, silver, and zinc in tin metal of commercial grades. The preparation of standards and samples by chill-casting of tin in open molds and in evacuated tubes is described. The use of a press is found convenient in forming electrodes from tin metal. The characteristics of the tin spark under varied operating conditions are discussed in connection with the selection of optimum conditions of excitation. Application of the step sector provides a means of extending the range of line intensity measurements with the microphotometer as well as for plate calibration. Rapid reduction of the photometric measurements to intensities is made by a modified graphical calculator. The shapes of the analytical curves derived from measurements on tin standards are compared, and deviations from the ideal case are discussed. Repeated determinations on homogeneous samples show a standard deviation of from 1.0 to 2.5 percent. Single determinations in routine analysis are estimated to fall within 5 percent of the actual concentration, with few exceptions. The analyses are carried out on groups of six samples in a working time of 5 minutes per determination.

CONTENTS

I. INTRODUCTION

The National Bureau of Standards has been assigned the responsibility for testing a number of products of tin metal for conformity with Federal and departmental specifications of composition. Of major importance is the determination of impurities in fusible plugs

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[1] Presented at the Ninth Summer Conference on Spectroscopy and Its Applications at Massachusetts Institute of Technology, Cambridge, Mass., July 21-23, 1941.

employed as safety devices for boiler protection; other materials examined include tin pipe and tin linings of pipes and fittings, as well as samples of pig tin purchased by the Government. The problems presented by the analysis of tin have proved tedious and time-consuming for application of the usual wet-chemical methods, primarily because of the low concentrations of impurities involved, usually below 1 percent. For reasonable accuracy, the analyst requires rather large samples and must exercise painstaking care in the analytical operations.

The possibility that the spectrographic method of analysis might relieve the chemist of labor was recognized as early as 1922 by Meggers, Kiess, and Stimson [1],[2] of this Bureau, who described a method for estimating the impurities in fusible plugs. The method provided for visual comparison of the photographed spectral lines from the sample under test with the lines from samples of graded known composition. In the years intervening since the publication of this pioneer paper, a number of contributions have appeared in the literature on various aspects of the spectrographic analysis of tin. Gerlach [2] showed that the effects of variations in spectral exposure and in photography could be largely eliminated by referring the intensity of the impurity line to a neighboring line of the major constituent as standard. This principle, now known as internal control, was embodied in the method of homologous pairs applied to the analysis of tin by Negresco [3], Schweitzer [4], Gerlach [5], and Smith [6, 7]. Quantitative estimations were based upon observation of pairs of impurity and control lines. Each selected pair at equality of intensity could be relied upon to represent a definite concentration. The method is undoubtedly useful where photometric measurements are not made, but it is subject to the inconveniences and uncertainties of interpolation, especially when the available number of pairs of matching lines is small.

A distinct advantage resulted from application of the rotating logarithmic spiral sector to the comparison of line intensities in the analysis of tin. This method, in which the length of the wedge-shaped line image serves as a measure of the line intensity, was applied by Töpelmann and Shuhknecht [8] to the determination of lead in concentrations as high as 3 percent in tin. Hitchen [9] describes the determination by this method of antimony, arsenic, bismuth, copper, iron, lead, and zinc in tin, with deviations seldom exceeding 5 percent. This paper is especially recommended for its thorough discussions of line selection and of sampling problems. A recent paper by Stewart [10] describes a similar method for determining antimony, bismuth, copper, iron, and lead in commercial tin.

The development of the microphotometer and its use in spectrographic analyses provides a truly objective method of measuring relative spectral line intensities. The earliest mention of microphotometric measurements in tin analysis is found in a paper by Scheibe, Linström, and Schnettler [11], who describe the determination of lead in concentrations up to 9 percent. Follet [12] employed the microphotometer combined with a stepped wedge to provide calibration of the photographic plate and illustrated this procedure by the determination of lead in tin. In the range from 0.02 to 0.6 percent of lead, the probable error was reported to be ±1.5 percent for a single determination.

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[2] Figures in brackets indicate the literature references at the end of this paper.

All of the investigations mentioned have favored the excitation of the tin spectrum by the condensed spark discharge. The arc, however, has been employed by Smith [6], by Hitchen [9], by Breckpot [13], and undoubtedly by many others who have found it satisfactory for qualitative analysis and for quantitative estimation particularly in the range of low concentrations of impurities. Where both arc and spark excitation have been available, the spark has generally been found more reproducible and convenient.

At this Bureau an increasing burden of routine testing in the chemical laboratory led to renewed interest in the spectrographic method. A procedure was developed whereby the required determinations of impurities in tin could be made with a considerable saving in time and labor and with the requisite accuracy. The specifications under which the tin is tested are given in table 1; these are fixed mostly by the requirement for metal of high purity in many of the uses of tin. For example, impurities in fusible plugs may cause an increase in the melting point beyond the limit of safety protection of boilers [14]. Zinc is especially effective in raising the melting point of the plug in service, apparently by formation of a network of zinc oxide in the tin matrix. Tin piping for distilled-water lines must be free of impurities which might be absorbed by the water; a minimum concentration of lead is specified here because of the numerous chemical determinations of this element, in which contamination by lead must be avoided. The specifications call for the determination of a number of elements either explicitly, as in the case of Federal Specification QQ–T–371, or inferred in other cases where the minimum limit for tin involves the determination of the total of impurities. The major impurities encountered are copper, lead, arsenic, and antimony. In fusible plugs, copper and lead have been observed as high as 2 percent each. Other elements are generally below 0.1 percent. The analytical problem therefore involves both the requirement for the precise determination of the major impurities and the requirement for a degree of sensitivity sufficient to permit certain determinations as low as 0.01 percent or less. In addition to achieving the desired accuracy and sensitivity, it was proposed to simplify the manipulations, as far as possible, to realize the potential advantages of speed and convenience in the spectrographic method.

TABLE 1.—*Specifications for metallic tin*

Source of specification	Material	Sn, min	Pb, max	Sb, max	Zn, max	Cd, max	As, max	Cu, max	S, max	Fe, max	Bi, max
		%	%	%	%	%	%	%	%	%	%
Federal Government QQ–T–371.	Pig tin, grade *A*.	99.75	0.10	0.10	None [1]	None [1]	0.10	0.10	0.01	0.01	0.01
Federal Government QQ–T–371.	Pig tin, grade *B*.	98.00	1.50	1.50	do. [1]	do. [1]	.10	.10	.01	.10	.10
U. S. Department of Commerce, Bureau of Marine Inspection and Navigation.	Fusible safety plugs.	99.3	.10	----	0.10	----	----	.50	----	----	----
U. S. Department of Commerce, National Bureau of Standards.	Block tin pipe	99.9	.03	----	----	----	----	----	----	----	----
U. S. Department of Agriculture, Bureau of Agricultural Chemistry and Engineering.	Linings of pipes and fittings.	99.9	.09	----	----	----	----	----	----	----	----

[1] "As determined on a 20-g sample." It is assumed that this is equivalent to less than 0.01 percent.

The author, surveying methods of comparing spectral line intensities [15], described preliminary results on the use of the step sector and plate calibration for the determination of copper in fusible tin plugs. This method has now been extended to cover the analytical requirements of the specifications outlined above except for the determination of sulfur. The measurement of a single spectral exposure suffices in most cases for the determination of 10 elements in tin—namely, antimony, arsenic, bismuth, cadmium, copper, indium, iron, lead, silver, and zinc. Reduction of photometric measurements to line-intensity ratios is made by a graphical calculator modified to permit rapid use with stepped spectra. The general procedure is adapted to the routine analysis of commercial metals, with a minimum chance of error on the part of the observer. It is the purpose of this paper to describe the procedure employed in the analysis of tin, with particular regard to sampling, preparation of standards, spark excitation, and photometry.

II. PREPARATION OF SAMPLES AND STANDARDS

1. SAMPLE RODS FORMED BY MELTING OR PRESSING

The form of the tin submitted for analysis cannot, in general, be controlled. A typical group of samples is shown in figure 1. The majority of the samples submitted for test are fusible plugs (group *C* of fig. 1) in which the tin core, heated in contact with the brass casing during manufacture, is known to absorb varying amounts of the constituents of the brass. The procedure previously employed to provide a homogeneous sample for chemical analysis was to melt the tin from the casing, to catch it in a warm crucible, and, finally, to cast it in a cold mold. A similar procedure was followed in obtaining the spectrographic sample, but the design of the mold was modified to produce a two-fingered casting from which short rods suitable for spark electrodes could be cut. The first castings provided rods ⅛ in. in diameter; later the diameter was increased to ¼ in. to realize the advantages gained in sparking a larger electrode area. To obtain electrodes, two pieces of the rod at least ½ in. long are cut from the casting and the ends to be sparked are turned flat on a lathe. The cast specimens exhibit a high degree of homogeneity, as will be shown later by the results obtained.

Samples in forms other than fusible plugs formerly were fabricated into rods by melting and casting a few grams of turnings in glass tubes, sealed under vacuum. This lengthy procedure has recently been replaced by compressing the turnings, millings, or scrapings into small rods for electrodes. A commercially available hydraulic pressing machine is used to prepare two 2-g rods, ¼ in. in diameter and 5/16 in. long. The spectra of electrodes prepared from castings and from compressed drillings of the same sample were compared to observe any significant differences, as illustrated in figure 2. Apparently the only differences are those caused by contamination of the sample, not during the pressing operation, but in the machining and handling of the turnings. The maximum observed increase in iron was 0.004 percent when fine turnings were cut. The extraneous impurities may be removed by washing the turnings in dilute hydrochloric acid. Where preparation of the sample can be controlled, a more satisfactory procedure is to use a tool made of a material which will not interfere in the analysis, for example, tungsten carbide. The magnesium in-

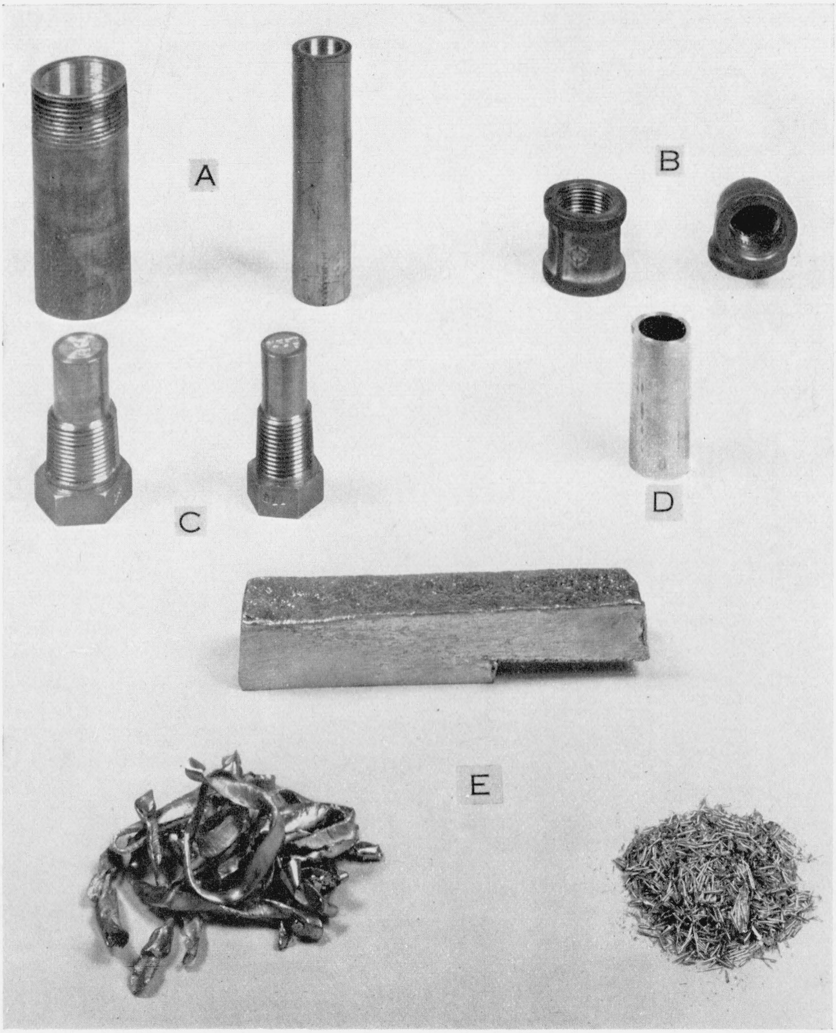

FIGURE 1.—*Typical samples submitted for analysis of tin.*

A, Tin-lined copper and brass pipe; *B*, tin-lined fittings; *C*, tin fusible plugs in brass casings; *D*, block tin pipe; *E*, samples of pig tin in various forms.

troduced in handling the turnings can easily be avoided. The usual rules of representative sampling should be obeyed in obtaining the portion for analysis.

The pressed rod provides an electrode sparking surface composed of several turnings, which is an advantage in obtaining an average sample. The prepared set of electrodes will provide a number of spectral exposures when machined to a clean surface after each run.

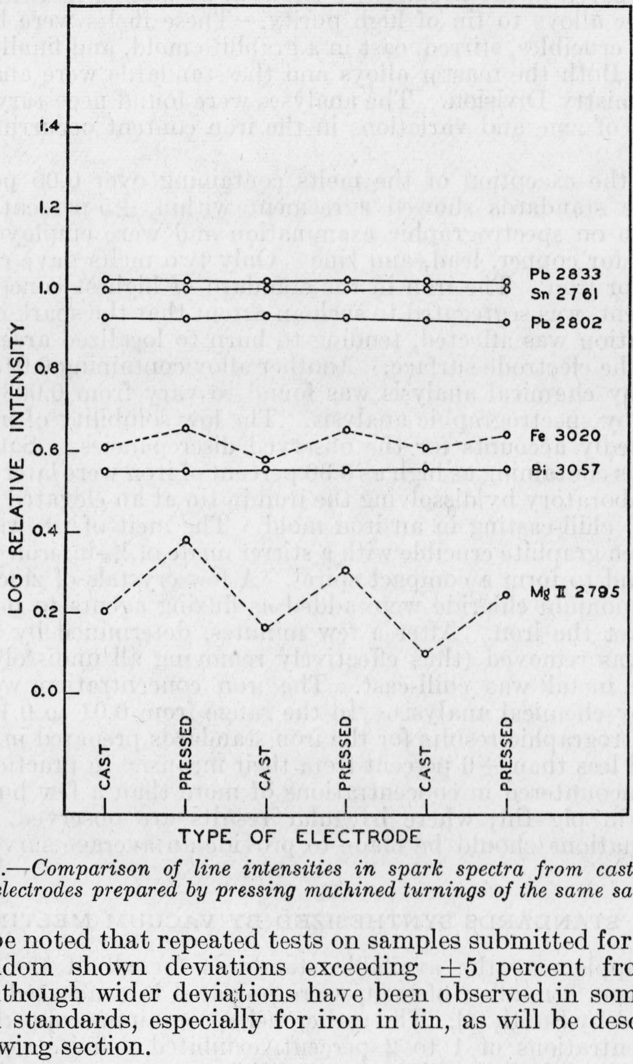

FIGURE 2.—*Comparison of line intensities in spark spectra from cast electrodes and electrodes prepared by pressing machined turnings of the same sample.*

It may be noted that repeated tests on samples submitted for analysis have seldom shown deviations exceeding ±5 percent from their mean, although wider deviations have been observed in some of the prepared standards, especially for iron in tin, as will be described in the following section.

2. CHEMICALLY ANALYZED STANDARDS

Reference standards of tin metal containing known concentrations of impurities were obtained by (1) selection of samples previously analyzed by chemical methods, (2) melting the constituents in an open crucible and casting in rod form, followed by chemical analysis, and (3) melting weighed amounts of the constituents in glass tubes sealed in vacuum. Samples analyzed by routine chemical methods in this Bureau were found in good agreement on spectrographic examination, except for a few determinations of small concentrations of the order of 0.05 percent or less. To cover the required ranges of concentrations, melts of tin containing copper, iron, lead, and zinc were prepared in the Metallurgy Division by adding known amounts of master alloys to tin of high purity. These melts were heated in graphite crucibles, stirred, cast in a graphite mold, and finally swaged to rod. Both the master alloys and the standards were analyzed in the Chemistry Division. The analyses were found necessary because of losses of zinc and variations in the iron content occurring during melting.

With the exception of the melts containing over 0.05 percent of iron, the standards showed agreement within ±5-percent average deviation on spectrographic examination and were employed in the analysis for copper, lead, and zinc Only two melts gave consistent results for iron. The iron in the standard of highest concentration, 0.3 percent, was segregated to such an extent that the spark employed in excitation was affected, tending to burn to localized areas high in iron on the electrode surface. Another alloy containing 0.015 percent of iron by chemical analysis was found to vary from 0.008 to 0.040 percent by spectrographic analysis. The low solubility of iron in tin undoubtedly accounts for the observed discrepancies.[3] Satisfactory standards containing as high as 0.36 percent of iron were later obtained in our laboratory by dissolving the iron in tin at an elevated temperature and chill-casting in an iron mold. The melt of tin was stirred in an open graphite crucible with a stirrer made of 1/16-in. iron wire bent at the end to form a compact spiral. A few crystals of zinc chloride and ammonium chloride were added as fluxing agents to permit the tin to wet the iron. After a few minutes, determined by trial, the stirrer was removed (thus effectively removing all undissolved iron) and the metal was chill-cast. The iron concentration was determined by chemical analysis. In the range from 0.01 to 0.1 percent, the spectrographic results for the iron standards prepared in this way deviated less than ±6 percent from their means. In practice, iron is rarely encountered in concentrations of more than a few hundredths percent in pig tin; where irregular results are observed, repeated determinations should be made to provide an average survey of the sample.

3. STANDARDS SYNTHESIZED BY VACUUM MELTING

To supplement the available standards for all of the elements except iron, a number of melts were prepared in evacuated tubes, as suggested by Smith [6]. The earlier melts, containing copper and lead in concentrations of 1 to 2 percent, exhibited definite segregation. The extreme deviations in spectrographic results amounted to ±10 percent along a casting in some cases, despite cooling of the well-mixed melt by an air blast. Improved results followed the adoption of half the quantity of metal for each melt (20 g) and cooling the

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[3] Phase relations in tin alloys are discussed in detail by Mantell [16].

melting tube by immersion in water. In general, the standards prepared by the latter method showed larger deviations caused by segregation than were observed for the same elements in the chill-cast samples. However, this did not preclude their use, since the average of the spectral measurements made at various points (usually four) on the bars gave values in agreement with the chemically analyzed standards. The analytical data for antimony, arsenic, bismuth, indium, and silver are based entirely on the vacuum-melted standards.

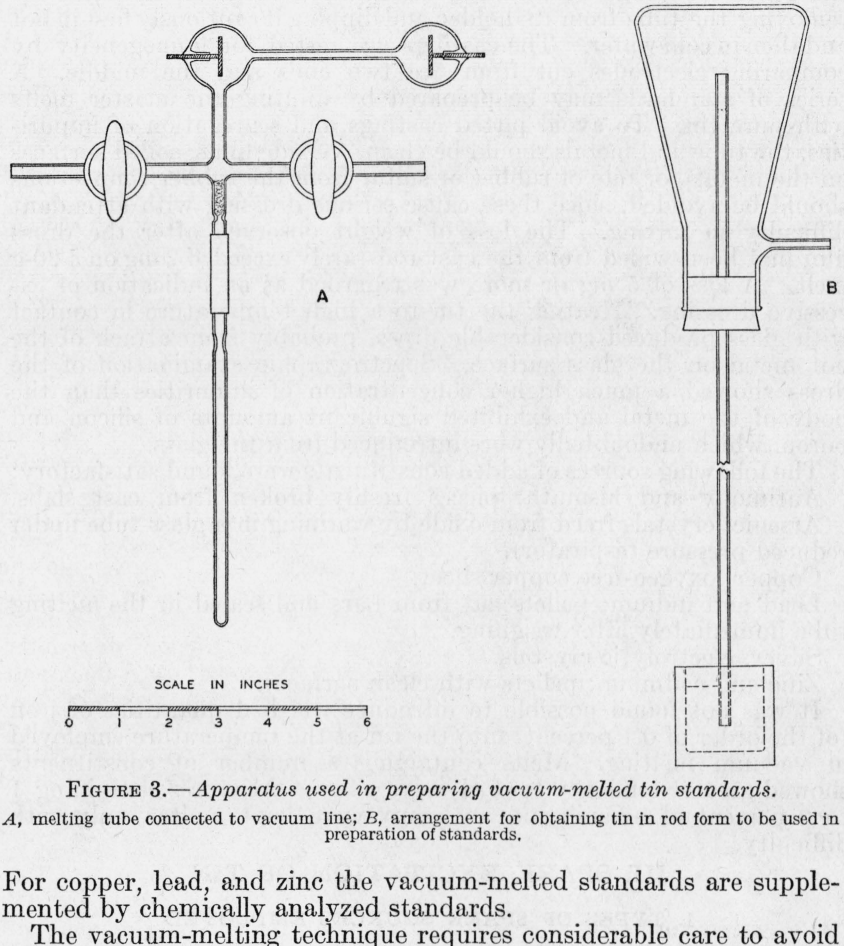

FIGURE 3.—*Apparatus used in preparing vacuum-melted tin standards.*

A, melting tube connected to vacuum line; *B*, arrangement for obtaining tin in rod form to be used in preparation of standards.

For copper, lead, and zinc the vacuum-melted standards are supplemented by chemically analyzed standards.

The vacuum-melting technique requires considerable care to avoid time-consuming failures. The procedure found most suitable will be described in detail for the benefit of those contemplating similar operations. A convenient arrangement for vacuum melting is shown in figure 3. Tin rod of diameter slightly less than that of the final melting tube, ¼ in. (fig. 3, *A*), is prepared by drawing the molten metal up in a glass tube by suction, as demonstrated in figure 3 (*B*). The glass is broken from the cast rod only when the metal is required. The weighed amount (20 g) of this rod and the other constituents are placed in the glass melting tube closed at one end. After a constriction is made above the charge, the tube is attached by a rubber connector to the vacuum line, as shown in figure 3 (*A*). The contents of the melting tube are protected from contamination by a wad of glass wool. The discharge tube, excited by a small sign-lighting transformer, acts as a simple vacuum gage. After evacuation, the melting tube is sealed off neatly at the constriction, placed in the open end of a long U-shaped wire holder, and heated carefully in a large flame. The melted charge is mixed by pouring from one end of the tube to the other for about 15 minutes, after which the melt is cooled by removing the tube from its holder and dipping it cautiously first in hot and then in cold water. The castings are tested for homogeneity by comparing electrodes cut from the two ends and the middle. A series of standards may be prepared by diluting the master melts with pure tin. To avoid pitted castings and segregation of impurities, the tube and metals should be clean. Oxide films, soiled surfaces on the metals, or bits of rubber or sulfur from the rubber connections should be avoided, since these cause serious drossing with attendant difficulty in mixing. The loss of weight observed after the dross film had been wiped from the cast rod rarely exceeded 2 mg on a 20-g melt. A loss of 5 mg or more was regarded as an indication of excessive drossing. Heating the tin to a high temperature in contact with glass produced considerable dross, probably from attack of the hot metal on the glass surface. Spectrographic examination of the dross showed a much higher concentration of impurities than the body of the metal and exhibited significant amounts of silicon and boron, which undoubtedly were introduced from the glass.

The following sources of added constituents were found satisfactory:

Antimony and bismuth: pieces freshly broken from cast slabs.

Arsenic: crystals freed from oxide by warming in a glass tube under reduced pressure (aspirator).

Copper: oxygen-free copper sheet.

Lead and indium: pellets cut from bars and sealed in the melting tube immediately after weighing.

Silver: electrolytic crystals.

Zinc and cadmium: pellets with clean surfaces.

It was not found possible to introduce weighed quantities of iron (of the order of 0.1 percent) into the tin at the temperature employed in vacuum melting. Melts containing a number of constituents showed greater tendency toward segregation. Mixtures containing 1 to 2 percent of arsenic and antimony were kept molten only with difficulty.

III. SPARK EXCITATION OF TIN

1. TYPES OF SPARK SOURCES EMPLOYED

The high-voltage condensed spark was found sufficiently sensitive, as well as reproducible, for the requirements of this analysis of tin. Both the simple spark circuit and the spark circuit with synchronous interrupter have been employed with satisfactory results. The simple oscillating circuit was fed by a 1-kva 15,000-volt transformer operated with a current of 2.50 to 2.55 amp in the primary. A condenser bank of capacitance 0.0030 μf and an inductance[4] of 19 μh were in the

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[4] The inductance in the spark circuits was calculated from measurement of the capacitance of the condensers and the frequency of oscillation of the circuit, both measurements being made by direct-reading meters. The resistance in the circuit was assumed to be negligible, and the value of inductance, L, was calculated from tabulated values of LC for various frequencies, based on the formula $\lambda=1884\sqrt{LC}$.

circuit with the spark in the secondary. With this low power, the spark gave a steady discharge with very uniform attack on the electrodes; however, an exposure time of 2 minutes was required to provide sufficient strength in the spectrum. Later, a commercial 2-kva spark unit equipped with a synchronous interrupter was installed in the laboratory, since a source of higher power was desired for work on other problems. This unit, equipped with controls to facilitate the change from one set of operating conditions to another, was found convenient for studies of the tin spark.

2. EFFECTS OF OPERATING CONDITIONS

The general characteristics of spark discharges have been extensively investigated by Kaiser and others [17, 18]. It is of importance to examine the particular characteristics of the tin spark to establish optimum conditions for analysis. The observations to be described were made on a spark between tin electrodes separated by a gap of 4 mm and fed by the interrupted spark circuit. The electrodes were cylindrical, having a diameter, at first, of 5 mm, and later of ¼ in. (6.4 mm); the ends were turned flat and edges slightly beveled. Electrodes of this shape are easily faced on a lathe and conform to the shape recommended by Kaiser for spark electrodes.

The choice of power for this spark is limited by the low melting point of the metal; excessive power produces marked distortion of the surface of the electrodes, finally resulting in fusion of the ends. The power chosen was 2/3 kva with a capacitance of 0.0090 μf. The addition of inductance to the circuit, as is well known, suppresses the spark-like characteristics of the discharge, that is, decreases the intensity of spectral background, air lines, and lines from ionized atoms. To establish an optimum value of inductance, the effect of its increase on the intensities of the spectral lines was determined as shown in figure 4. The apparatus provided four steps of 24, 60, 152, and 335 μh. The expected reduction of intensity of ionized atoms is shown by the sharp drop in the intensity of Sn II 2896A; this is accompanied by a decrease in background intensity. For the lines of neutral atoms, however, an increase in intensity is observed between 24 and 152 μh almost diametrically opposed to the decreased intensity of the Sn II line. The further increase of inductance from 152 to 335 μh resulted in little change in the intensity of lines of neutral atoms, but the spark lines and background were further reduced. The attack of the spark on the electrodes varies considerably with the amount of inductance. At the lowest inductance the electrode surface is only partially burned in a ringlike area near the edge. As the inductance is increased, a more uniform attack of the electrodes results until at values of 152 or 335 μh the surface is almost uniformly pitted.

The fact that added inductance up to 152 μh produced an increase in the intensity of lines of neutral atoms, at the expense of lines of ionized atoms and background, indicated that higher sensitivity of detection of minor impurities would be attained with higher inductance. This was confirmed by tests with samples of low concentration of impurities. Consideration of the requirements for sensitivity and freedom from background indicated a choice of one of the higher values of inductance for the analysis.[5] Studies of reproducibility showed little difference between the last two steps of inductance. The highest value, 335 μh, was adopted in view of the slight gain in the intensity of most of the lines over background.

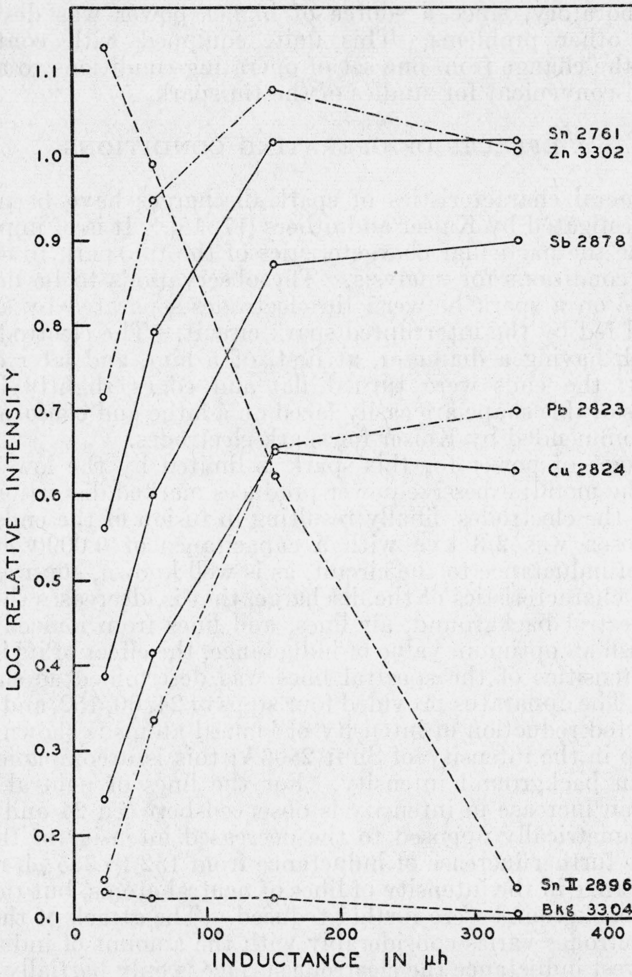

FIGURE 4.—*Effect of variation of inductance in the spark circuit on the intensities of spectral lines and background.*

As a factor in the reproducibility of the measurements, it is of importance also to observe the effects of variation in inductance on the intensity ratios of the line pairs chosen for the analysis. In figure 5 this effect is observed to be small for the analytical line pairs

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[5] Previous observers have differed widely in their choice of inductance for the tin spark, and in one case recommendation was made that inductance be omitted entirely to obtain higher sensitivity. It is obvious that the effect of inductance will depend on the other variables in the circuit, and therefore the optimum amount of inductance should be determined for the particular conditions employed. In any case, however, the inclusion of a moderate amount of inductance for the analysis of tin is indicated from results obtained in this laboratory on both the simple and interrupted spark circuits.

shown, especially at the higher values of inductance. Similar behavior was observed for the other spectral lines chosen for the analysis.

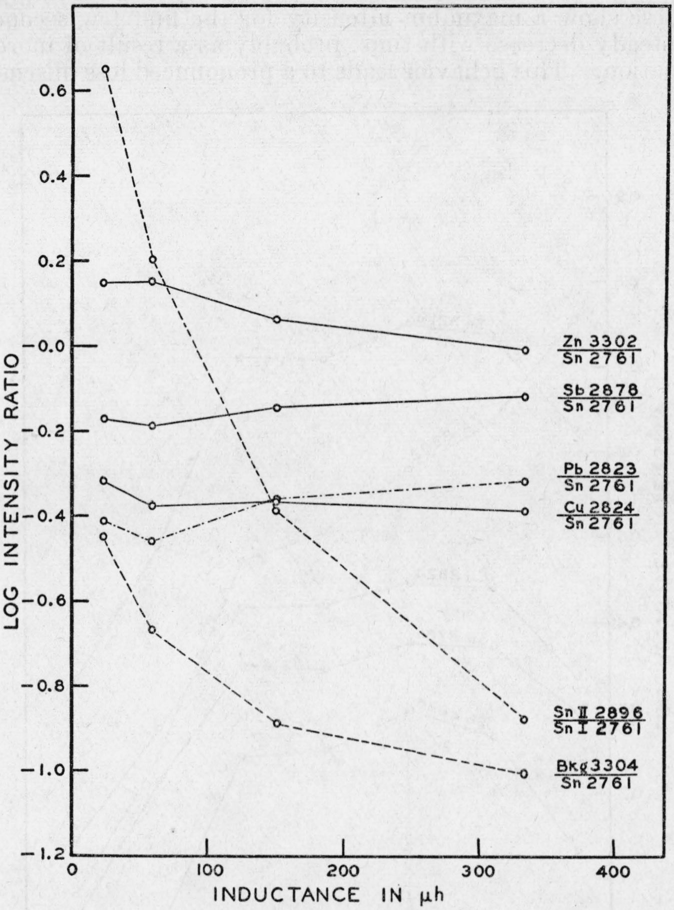

FIGURE 5.—*Effect of variation of inductance in the spark circuit on the ratio of spectral line intensities.*

3. CHARACTERISTICS OF THE SPARK ADOPTED

The tin spark, under conditions of high inductance, produces a spectrum closely resembling that of the arc and, in fact, the excitation may be described as a controlled arc. It is of interest to observe the change in spectral radiation during the discharge period, as shown in the typical case illustrated in figure 6. The discharge is characterized by three stages: (1) a short induction period of generally increasing line intensity in which the vapors of the spark gap approach an equilibrium condition; (2) a period 4 or 5 times as long, depending on the area of the electrode, in which the intensities of most of the lines are at a maximum and show little change in relative values; and (3) an abrupt decrease in the intensities of the lines as the discharge is weakened and confined to one spot on the electrode, apparently by the surface film of oxide which is formed on the electrode surface. The behavior of zinc lines is markedly different from the general case; these show a maximum intensity for the first few seconds and then a steady decrease with time, probably as a result of more rapid volatilization. This behavior leads to a pronounced loss of sensitivity of zinc when the electrodes are sparked for an interval before the exposure is made. The effect of oxidation of tin electrodes in reducing the intensity of the spark has been observed by Töpelmann and Shuhknecht [8], who measured the variation in current in the oscillating circuit with time of sparking. Their curves indicate a rise and fall of current during the first minute of sparking, which is similar to the rise and fall of the line intensities in the "normal" cases of copper, lead, and tin in figure 6.

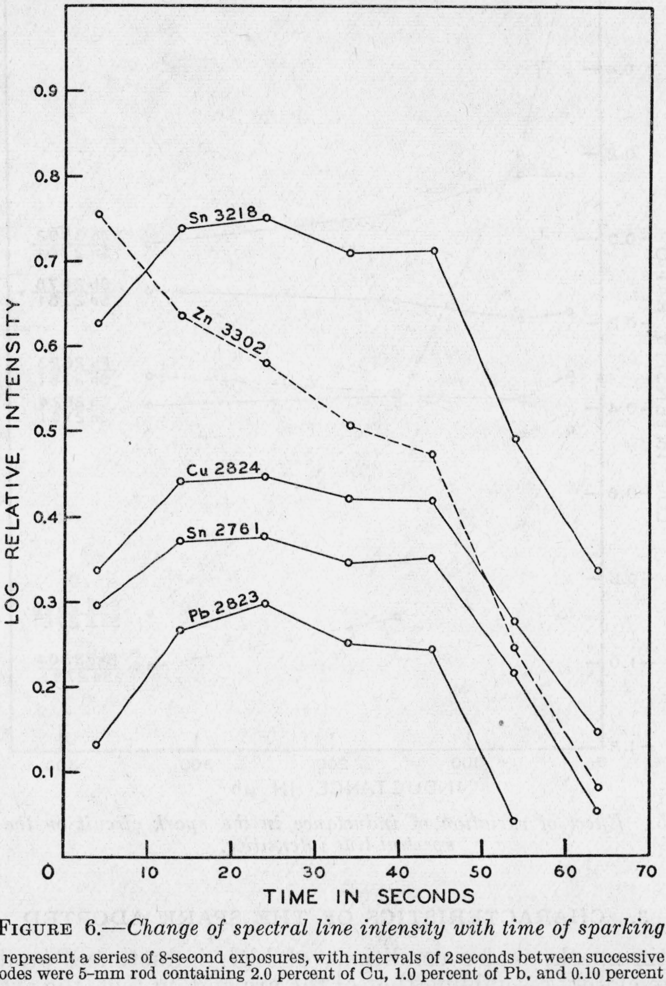

FIGURE 6.—*Change of spectral line intensity with time of sparking.*

The points represent a series of 8-second exposures, with intervals of 2 seconds between successive exposures. Electrodes were 5-mm rod containing 2.0 percent of Cu, 1.0 percent of Pb, and 0.10 percent of Zn.

Ideally, the second phase of the discharge would appear most reproducible for the determination of copper in lead. In practice, however, the exposure time is adjusted to cover both the first and second phases of the sparking cycle to provide sufficient line strength for the detection of minor impurities. With ¼-in. electrodes, oxidation of the electrodes becomes effective in reducing the line intensity, only after 1 minute; the exposure is limited to this interval.

Changes in other variables in the spark circuit—such as output energy, controlled by the synchronous interrupter, and the gap distance between the electrodes—affect the over-all intensity of the spectrum and are kept constant to minimize photometric errors. The intensity ratios of copper, lead, and bismuth lines to tin internal control were found to be little affected by changes in the adjustment of the interrupter; zinc showed a noticeable variation. The constants of the circuit now employed are summarized as follows:

Circuit: Commercial spark unit, 35,000-volt transformer feeding an oscillating circuit across a condenser. This circuit consists of the condenser connected to a solenoidal induction coil, a rotary interrupter run by a synchronous motor, and the spark gap.
Input voltage: 106 volts.
Power: 2/3 kva.
Capacity of condensers: 0.0090 μf.
Inductance of circuit: 335 μh.
Interrupter adjustment: Intermediate between the positions for high energy and low energy in circuit (40–42 volts on the indicating instrument furnished with the unit).
Electrode form: Two electrodes of circular rod ¼ in. (6.4 mm) in diameter, turned flat on discharge ends, and edges slightly beveled. Length not less than ¼ in.
Electrode holder: Heavy metal spring clips.
Electrode gap distance: 4 mm.
Exposure time: 1 minute, no prespark.

IV. ANALYTICAL PROCEDURE

1. THE SPECTROGRAPH AND ITS ILLUMINATION

A spectrograph of moderately high dispersion, although not essential to certain determinations in metallic tin, nevertheless provides the advantages of reduced background intensity and wider separation of lines. This is especially important when the spectrograph slit is widened for accurate photometric measurements. A large Littrow quartz-prism spectrograph of focal length $f_D=183$ cm was employed throughout the work.

The simplicity of the tin spectrum, which is an advantage in avoiding interferences of lines, is a disadvantage when selecting tin lines of suitable low intensity for internal control. In order to utilize the available tin lines over the various ranges of concentrations of the impurities, a reduction of the intensity of the lines is accomplished by means of a step sector rotated at the slit of the spectrograph. In addition, the step sector provides a line pattern of intensities for calibrating the photographic plate [19]. Proper use of the sector requires uniform illumination of the sector and slit combination. For this, an image of the source is focused on the spectrograph collimator lens by a lens at the slit of the spectrograph. The sector is mounted close to the slit. The system, which provides uniform illumination over about 1 cm of the slit length, is illustrated in figure 7.

An image of the full spark column (spark gap 4 mm) is focused on the collimator lens of the spectrograph by means of a thin crystal quartz lens, L_1 (1-mm edge thickness, 2.5-cm diameter, and focal length f_D=34 cm), mounted in the cover of the slit, *S*. Since the focal length of lens L_1 determines the distance of the spark source, *X*, from the slit, a focal length was chosen which provides the requisite uniformity of slit illumination without too great a loss in light intensity. The step sector, *R*, made in the Bureau shop, has 5 steps each 2 mm high cut in the periphery of the disk, the ratio of successive steps being 1.585, so that the logarithm of the ratio is the simple value 0.200. The sector disk is mounted as close to the slit cover, *D*, as possible (0.5 mm) and rotates at a speed of 1,700 rpm. The position of the spark source, *X*, for the spectral region 2700 to 3400 A, is fixed by photographing full-length images of the slit for successive displacements of the source and choosing that position of the source which provides most nearly uniform intensity along the slit image. An auxiliary lens, L_2, behind the spark stand, projects an enlarged image of the electrodes to a marked position on the screen, *I*, permitting rapid and accurate adjustment of both the position of the spark on the optical axis and the gap distance between the electrodes. The spectrograph slit is opened to 40 microns.

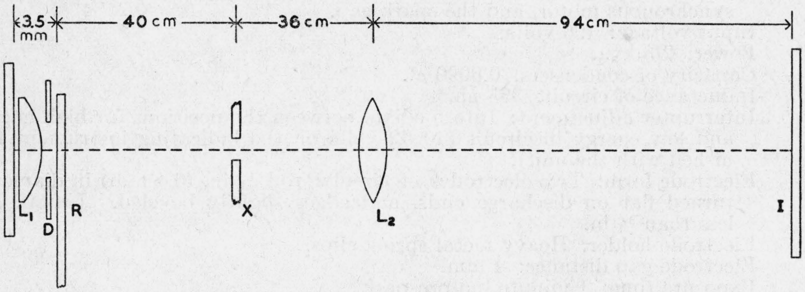

FIGURE 7.—*Diagrammatic sketch of the illuminating system employed with the spectrograph.*

The spectra of six samples, each exposed for 1 minute through 5 steps of the sector, are photographed on a 4- by 10-in. Eastman Spectrum Analysis Plate No. 1. The plate is developed in D–11, M–Q developer, with fixed time (2 min) and temperature (20°C). Uniform agitation was found especially important in obtaining reproducible results with this plate; the Eastman Process plate previously used (with twice the developing time) was much less sensitive to irregular agitation. Improved results were observed with a mechanically operated rocking device for the development.

2. CHOICE OF SPECTRAL LINES FOR ANALYSIS

Typical spectrograms of tin are reproduced in figure 8. The 2 samples represented by these exposures together contained the 10 elements determined by this procedure. The lines selected for the determination of impurities are marked on the illustration and a list is given in table 2. The choice of lines for the determinations of the lower concentrations of the impurities is limited to those disappearing

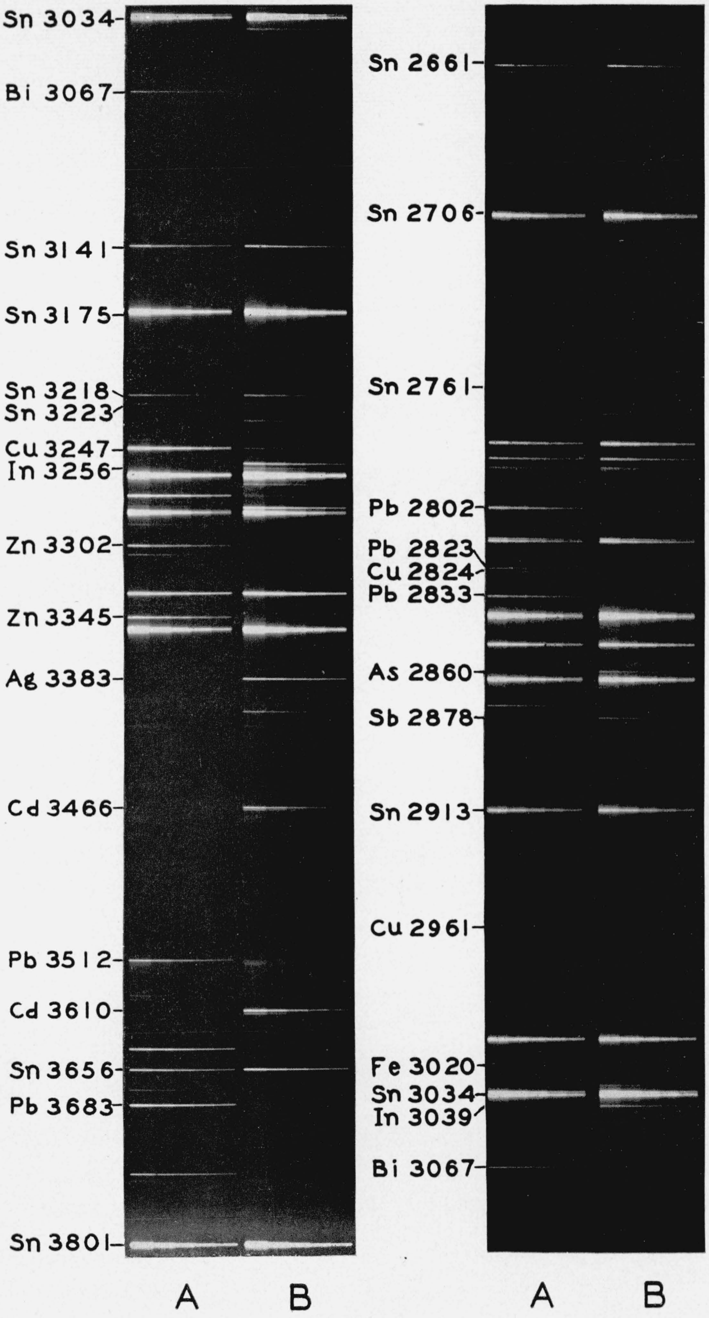

FIGURE 8.—*Typical spectrograms of tin samples.*

A, Sample containing 2.0 percent of Cu, Pb, and 0.2 percent of Bi, Zn; *B*, sample containing 2.0 percent of As, Sb, and 0.2 percent of Ag, Cd, In. A trace of iron is present in both samples.

last as the element is progressively diluted in tin. They are usually the strongest lines produced by neutral atoms of the impurities in the spectral region chosen as most convenient for analysis, 2600 to 3600 A. For higher concentrations of copper and lead (above 0.1 percent), the most sensitive lines of these elements were too intense for accurate photometric measurement and the weaker lines, Cu 2824 A and Pb 2823 A, were selected. In combination with Sn 2671 A, as internal control, the intensity ratios obtained with the two lines exhibited a high degree of precision. Marked similarity was observed in the behavior of the radiations during the sparking cycle previously described. In addition to the Sn 2761 A, a survey of the tin spectrum in this region reveals only two more lines of tin at the low level of intensity suitable for internal control lines. These tin lines, 3218 and 3223 A, may be employed as controls for the group of impurity lines at 3300 A. The line 2761 A was found most generally applicable, lying near the important group of impurity lines at 2800 A for several of the elements determined. This line is free from interference with other lines with the exception of iron 2761.78 A, which adds perceptible intensity to the tin line at iron concentrations above 0.04 percent. Iron has not been observed higher than 0.03 percent, and was usually below 0.01 percent, in many hundreds of determinations. The probability of interference of iron with the tin line is slight.

TABLE 2.—*Wavelengths employed in the analysis of tin*

Element	Wavelength	Concentration range	Remarks
	A	%	
Antimony	2877.92	0.06 to 2.0	
Arsenic	2860.45	.06 to 2.0	Wing of Sn 2863 A affects intensity measurements of this line.
Bismuth	3067.72	.001 to 0.2	
Cadmium	3466.20	.01 to 0.2	
	3610.51	<.01	Used for qualitative detection.
Copper	2824.37	.1 to 2.0	Avoid confusing this line with Pb 2823 A.
	3247.54	.001 to 0.05 (0.03 to 0.3).	Requires a weaker exposure (e. g., 30 sec) to cover the higher concentration range.
Indium	3039.36	.01 to 0.2	
	3256.09	.002 to 0.2	
Iron	3020.6d	.01 to 0.4	Most sensitive for iron in this region.
Lead	2802.00	.01 to 0.5	
	2823.19	.1 to 2.0	Avoid confusing this line with Cu 2824 A.
	2833.07	.003 to 0.5	Wing of Sn 2839 A affects intensity measurements of this line below 0.01 percent of Pb.
Silver	3382.89	.002 to 0.03	
Zinc	3302.8d	.01 to 0.2	Avoid confusing this line with Cu 3307.95 A.
	3345.57	<.01	Used for qualitative detection.
Tin	2761.78	Internal control line	Most generally useful control line, but iron line interferes above 0.04 percent of Fe.
	3218.68	do	
	3223.57	do	

3. PHOTOMETRIC MEASUREMENTS

The line blackenings on the photographic plate are measured by a commercial microphotometer modified [15] to provide ease and accuracy in measurement. The blackening deflections, as defined by Thomson and Duffendack [20], are observed by means of a barrier-layer cell and galvanometer on a scale from zero corresponding to the clear plate reading to 310 mm for the dark cell (opaque shutter). The important requirement that the full-scale deflection (zero reading) should remain unchanged during the series of measurements on a plate is met by drawing power for the 200-watt projection lamp from a large battery. After an initial stabilization period of about 15 minutes, the full-scale deflection becomes practically constant, except for a slight drift (1 mm in ½ hour) caused by cell fatigue.

The photometric procedure, in common with other methods involving plate calibration, consists in making two related series of measurements. First, to provide a plate-calibration curve, blackenings are measured for the consecutive steps of two or more line images selected to cover the blackening scale. The blackening values are plotted against the corresponding logarithms of the relative exposures calculated from the sector aperture ratios, and a smooth curve is drawn. For purposes of analysis, the exposure scale may be considered equivalent to an intensity scale, thus permitting conversion of blackening measurements to intensities.

The second series of measurements on the plate is that of the lines selected for analysis. Since a choice of blackenings in two or more steps of the stepped image may be possible, those measurements are favored which fall in the central part of the blackening scale. Usually two blackenings are measured for two consecutive steps of the line image. The recorded blackenings of the lines are reduced to log I values by means of the calibration curve. For the pairs of lines employed in the determinations, subtraction of the log I values gives log I_1/I_2. Where the blackening of each of the two lines is not measured in the same sector step, a correction is applied.

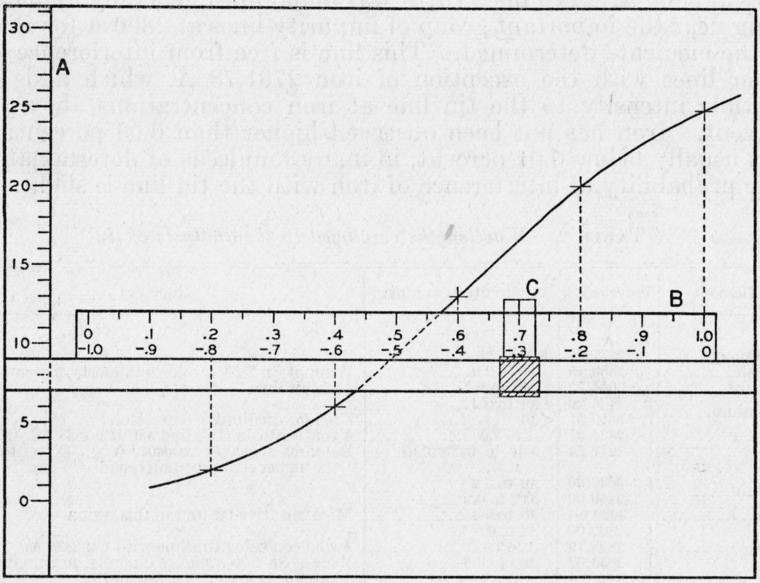

FIGURE 9.—*Graphical calculator used in rapid determination of log-intensity ratios from measured blackenings.*

These operations are laborious and subject to error if carried out by arithmetical calculation. The possibility of increasing the speed by means of a graphical calculator similar to that devised by Owens [21] was investigated. By changing the scales of a commercially available calculator, it was found possible to plot the calibration curve rapidly and then to read directly log I_1/I_2 for two lines, irrespective of the steps in the sectored image in which the individual blackenings are measured. A diagrammatic sketch of the calculator is given in figure 9. The ordinate scale, *A*, corresponds to the microphotometer scale, and the abscissa scale, *B*, to the logarithm of relative intensity. Scale *B* is movable horizontally along a rigid arm, which can be moved vertically. The plate-calibration curve is plotted from the blackening readings for Sn 2761 A in the five steps provided by the stepped sector. A typical section of a data sheet is shown in table 3. Since the logarithm of the aperture ratios of the successive sector steps is 0.200, step blackening values are plotted at the 0.200 intervals on the scale, as shown by the dotted lines on the diagram in figure 9. In practice the plotted points are checked by values from another line before the calibration curve is drawn. The determinations of log I_1/I_2 values from the blackening measurements of impurity and control lines are now made. The simplest case is one in which both blackenings are in the same step—for example, for Pb 2833 A and Sn 2761 A in step 3, as given in table 3. The arm, *B*, is raised to 13.1 on scale *A*, and scale *B* is moved sidewise until the zero value (left end of scale) lies at the intersection of the scale with the curve. An index marker, *C*, is moved over to this point to fix the position of the scale. The scale arm is then raised to 17.1 on scale *A*, and the reading at which the curve intersects scale *B* is recorded as log *I* Pb 2833/*I* Sn 2761. When the blackenings are measured in different steps, scale *B* is moved sidewise an interval of 0.200 or 0.400, depending on the relative apertures of the steps, before the log I_1/I_2 value is read. When the blackening of the impurity line, in the same step as the control, is lower than that of the control, the negative scale must be used. This is true also when the blackening of the impurity line is measured in a step of larger aperture than the control line. The recorded log I_1/I_2 values are applied to preestablished analytical curves to obtain the concentration of the impurity, which is entered in the column headed by the percent sign on the working sheet.

TABLE 3.—*Typical section of data sheet*

[Values in italics are log I_1/I_2 determined by graphical calculation from the measured line blackenings]

Wavelength	Step 1	Step 2	Step 3	Step 4	Step 5	Concentration
A	*cm*	*cm*	*cm*	*cm*	*cm*	%
Sn 2761	2.0	6.0	13.1	20.1	24.8	
Pb 2833	--------	10.0 *0.114*	17.1 *0.109*	--------	--------	0.178
Sb 2878	--------	--------	--------	--------	5.5 *−0.609*	.172
Ag 3383	15.0 *0.451*	--------	--------	--------	--------	.023

The operations with the calculator are more easily carried out than explained, and a considerable saving in time has resulted. The internal control line Sn 2761 A usually serves for plate calibration from 2700 to 3500 A, although above 3300 A the contrast of the plate increases. To avoid the construction of a second calibration curve for this region for the few measurements involved, the curve for Sn 2761 A is used under conditions which minimize the error. This is done by measuring the blackenings of the impurity lines near a fixed value on the lower end of the blackening scale where possible. When highest accuracy is desired for the lines affected (zinc, silver, and cadmium), internal control lines should be chosen near the impurity lines and the plate calibrated in this region.

To summarize the procedure, a single, sectored, spectral exposure is employed (1) to calibrate the plate by line images, (2) to provide usually two intensity measurements for each line, and (3) to provide accurate measurement of intensity ratios over a wider range than is possible with a single-step exposure.

4. ANALYTICAL CURVES

The measured values of log I impurity/I control are plotted for a series of known concentrations of the impurity to obtain the analytical curve for each impurity. Convenience in plotting is provided, as is customary, by constructing the analytical curve on semilogarithmic coordinate paper, with log I_1/I_2 values plotted on the linear scale and with percentage concentrations on the logarithmic scale. A typical analytical curve is shown in figure 10, constructed for the determination of lead between 0.01 and 0.2 percent. The points representing standards based on synthetic vacuum melts and others based on chemical analysis fall close to the smooth curve. The chemical value for the lead standard at 0.015 percent apparently was too high, but

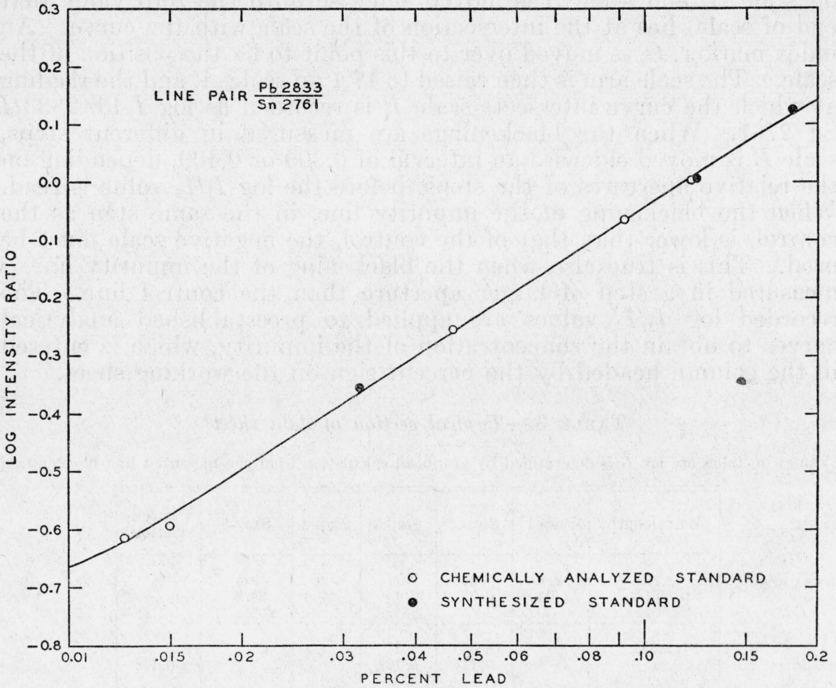

FIGURE 10.—*Typical analytical curve.*

Determination of lead between 0.01 and 0.2 percent in tin.

the deviation from the curve is only 0.001 percent; the agreement in general indicates a high accuracy in the chemical determinations. Similar curves were obtained for the other impurities. The agreement of the plotted points with the analytical curves in the more important ranges of concentrations is exhibited in table 4. For the ranges covered, the average deviation of the points from the curve is of the order of ±2.5 percent and the extreme deviations were within ±5 percent with few exceptions. A few standards showing abnormal disagreement on repeated measurement were discarded.

TABLE 4.—*Agreement of plotted points, based on standards, with the analytical curve*

Element	Wavelength (Sn 2761 control)	Concentration range	Average deviation of standards from curve
	A	%	%
Antimony	2877.92	0.1 to 2.0	±1.6
Arsenic	2860.45	.1 to 2.0	±2.5
Bismuth	3067.72	.003 to 0.1	±2.5
Cadmium	3466.20	.01 to 0.2	±2.0
Copper	2824.37	.2 to 2.0	±2.5
Indium	3256.09	.004 to 0.2	±4.2
Iron	3020.6d	.01 to 0.05	±2.4
Lead	2823.19	.01 to 2.0	±2.3
Lead	2833.07	.006 to 0.4	±3.3
Silver	3382.89	.002 to 0.2	±3.2
Zinc	3302.8d	.01 to 0.2	±2.4

The determination of the impurity is made by applying the value of the log I_1/I_2 ratio to the curve to find the concentration. The determination of the amount of tin in the sample, required by the specification for minimum tin content, is, of course, made by difference after the total concentration of the impurities is ascertained. In all cases the spectra are examined qualitatively for possible impurities before photometric measurements are made. In testing samples under the specifications listed in table 1, p. 167, it is usually unnecessary to make photometric measurements for more than four elements. A single determination is deemed sufficient for each element in the analysis of fusible plugs when the sample meets the specification. A duplicate determination is made with an additional set of electrodes of the sample when the fusible plug fails to meet the specification. For other samples, prepared by less refined sampling conditions, two or more determinations are made per element to ensure an average value of the concentration.

The procedure set up for this analysis affords an opportunity to compare the behavior of a number of analytical curves for different chemical elements in the same matrix. The method of plotting the analytical curves described above is equivalent to plotting log I_1/I_2 against log concentration. If a given added increment in concentration produces an equivalent change in the intensity of the spectral line radiated by the vaporized metal, a linear relation should be obtained and has been observed in many cases in spectrographic analysis. Under ideal conditions the relation between log intensity and log concentration should be represented by a straight line, inclined at 45° to the log-concentration axis or, in other words, having a slope equal to unity. The curves established for the tin analysis in many cases are linear, having slopes which in a few cases approach but do not equal unity. In some cases marked deviation from linearity is

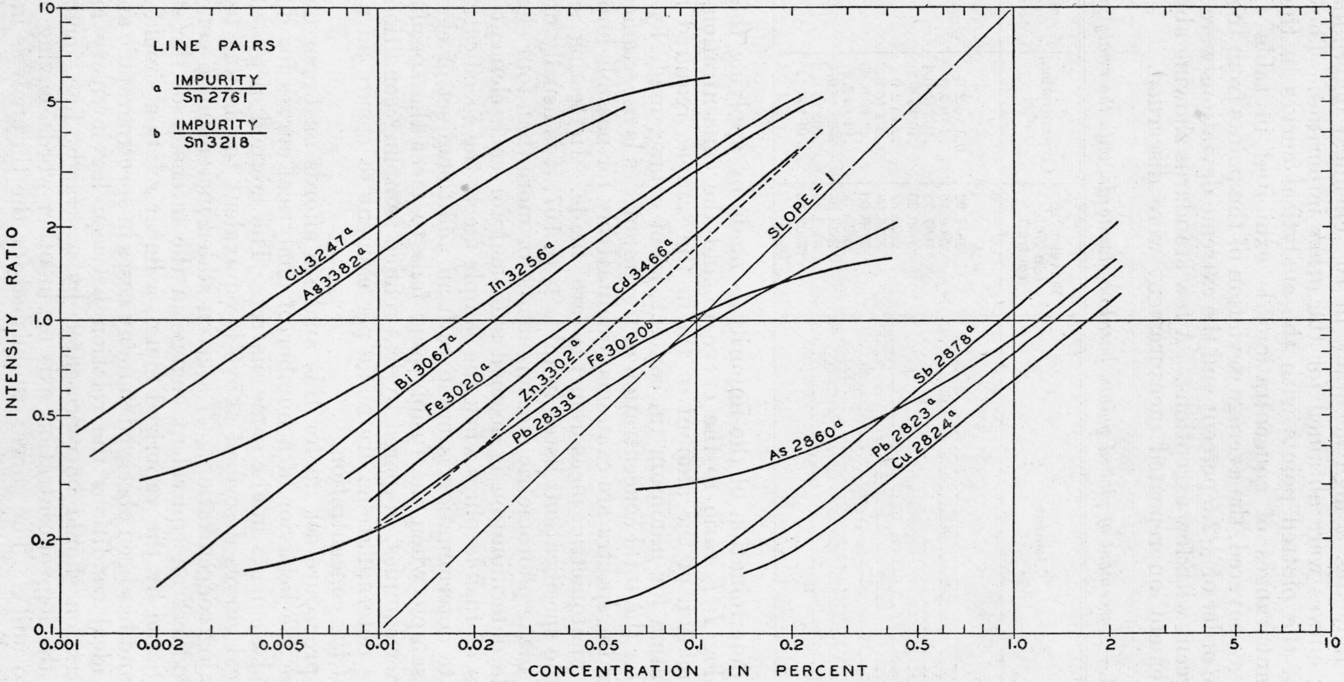

FIGURE 11.—*The system of analytical curves for the analysis of tin, arranged for intercomparison.*

observed. To illustrate the types of curves obtained, the 30 large-scale plots of the curves employed in the analysis of tin have been compressed to the scale of figure 11. A straight line of unit slope has been added for comparison. The closest approach to ideal behavior is shown for the zinc line 3302A, followed by Cd 3466A, Sb 2878A, Pb 2823A and Cu 2824A. Other lines exhibit either a smaller slope or a marked departure from linearity, or both. The different behavior of the various spectral lines is explained by two underlying causes: First, the presence of background in the spectrum which, when uncorrected, affects the photometric measurements of line intensities; and second, the tendency for certain radiations to lose energy by self-absorption in the vapors of the spark.

The effect of background in the spectrum in adding intensity to the spectral line becomes larger as the line intensity decreases with lowered concentration. This is observed in the plotted curves as a gradual decrease in slope at the lower end as the intensity of the line-plus-background approaches the background intensity asymptotically as a limit. Examination of the curves shows this effect in varying degrees, the most serious being observed for As 2860A, which, as previously mentioned, is measured on the background associated with Sn 2862A. Obviously the precision of the determinations will be adversely affected for these cases. A correction, by actual measurement of the background intensity, was not made because of the uncertainty involved. It was found preferable, when an accurate determination of arsenic is desired, to expose one or two standards on the same plate for reference under conditions which ensure comparable values of background.

The effect of self-absorption has been observed in spectographic analysis whenever an easily absorbed radiation, that is, one derived from a low-energy transition in the atom, is employed in determinations of concentrations of more than a few hundredths percent. This effect is observed here as a decreasing slope at the upper end of certain of the analytical curves. The shape of the curve for Cu 3247A above 0.02 percent indicates strong self-absorption, as might be expected from the nature of this line. Similarly, Ag 3383A exhibits the effect above 0.02 percent and, to a lesser degree, the deviation is observed for Bi 3067A above 0.04 percent, Fe 3020A above 0.05 percent, and Pb 2833A above 0.1 percent. In most cases these regions of decreased accuracy can be avoided; but, because of the scarcity of suitable spectral lines for copper, the line Cu 3247A is employed up to a concentration of 0.1 percent. The observation that curves fall roughly into two groups having different values for the slopes of their linear portions is probably related to the phenomenon of self-absorption. Those lines most affected by self-absorption fall into the class giving, in general, the smaller slope values, as will be seen by inspection of figure 11.

V. DISCUSSION

1. PRECISION AND ACCURACY

The precision of the method may be measured by the agreement of repeated determinations made on the same sample. To arrive at knowledge of the reproducibility of the spectrographic procedure independent of the effects of inhomogeneity in the sample, a carefully mixed and chill-cast sample is employed. The results of repeated determinations, on two photographic plates, for copper, lead, iron, and bismuth in the sample are shown in table 5. The results exhibit excellent reproducibility; the standard deviation ranges from 1.09 percent for copper to 2.52 percent for iron, the most troublesome case.

TABLE 5.—*Reproducibility of determinations on a single chill-cast sample of tin*

Plate number	Copper			Lead			Iron			Bismuth		
	Observed concentration	Deviation from mean	Percentage deviation	Observed concentration	Deviation from mean	Percentage deviation	Observed concentration	Deviation from mean	Percentage deviation	Observed concentration	Deviation from mean	Percentage deviation
	Pct.			*Pct.*			*Pct.*			*Pct.*		
1	0.670	0.003	0.4	0.132	0.001	0.8	0.0107	0.0004	3.9	0.00510	0.00001	0.2
	.677	.010	1.5	.133	.000	.0	.0106	.0003	2.9	.00517	.00008	1.6
	.662	.005	0.8	.132	.001	.8	.0103	.0000	0.0	.00507	.00002	0.4
	.681	.014	2.1	.137	.004	3.0	.0104	.0001	1.0	.00530	.00022	4.3
	.675	.008	1.2	.132	.001	0.8	.0103	.0000	0.0	.00510	.00001	0.2
	.658	.009	1.4	.132	.001	.8	.0103	.0000	.0	.00501	.00008	1.6
2	.665	.002	0.3	.134	.001	.8	.0097	.0006	5.8	.00497	.00012	2.4
	.661	.006	.9	.132	.001	.8	.0103	.0000	0.0	.00500	.00009	1.8
	.660	.007	1.0	.129	.004	3.0	.0100	.0003	2.9	.00494	.00015	2.9
	.662	.005	0.8	.137	.004	3.0	.0103	.0000	0.0	.00522	.00013	2.6
	.667	.000	.0	.132	.001	0.8	.0101	.0002	1.9	.00505	.00004	0.8
	.668	.001	.1	.129	.004	3.0	.0102	.0001	1.0	.00510	.00001	.2
Mean	.667			.133			0.0103			0.00509		
Average deviation		.0058	0.87		0.002	1.5		0.00017	1.6		0.00008	1.6
Standard deviation= $\sqrt{\Sigma D^2/n-1}$		.0073	1.09		0.0025	1.88		0.00026	2.52		0.00011	2.16

In routine analyses there are several factors involved which preclude attainment of this same degree of precision. In addition to the errors in photometric measurements previously discussed, an important factor is small-scale inhomogeneity in composition. To exhibit the degree of reproducibility of determinations on samples submitted for routine analysis, table 6 was prepared. This compares the results of duplicate determinations of copper and lead on a series of fusible plugs which failed to meet the specification. In most cases, the deviation between the pairs of values is well within 5 percent, and the mean should be good to ±2.5 percent. However, wider deviations have been observed in a few cases, for example the 19-percent deviation for copper in sample 9849. Segregation of copper in this sample, one of the first group to be analyzed spectrographically, was confirmed by further determinations. Precautions are now taken to provide more complete mixing of the sample before casting, to minimize errors from this source. Another factor which enters into considerations of precision is the day-to-day stability of the procedure. In preparing the analytical curves, a shift in the plotted values was observed as high as 3 percent over a period of several days. This is apparently caused by a variation in the excitation conditions which has not yet been explained. Where this shift might be important, as for determinations requiring the highest accuracy, a standard may be photographed on the plate with the unknown, to provide correction. In practice, when a sample fails to meet the specification, a second determination is made with a reliable standard for reference. A comparison of repeated runs of standards employed in this way over a period of weeks is shown in table 7, in which the agreement is usually within 6 percent except for iron, where segregation was apparent in the standards.

TABLE 6.—*Agreement of duplicate determinations on various samples of fusible plugs which failed to meet specifications*

Sample number	Copper			Lead		
	Observation 1	Observation 2	Deviation	Observation 1	Observation 2	Deviation
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
9761	0.53	0.52	1.9	0.063	0.063	0.0
9798	.70	.67	4.4	1.30	1.17	10.7
9849	.174	.21	19.0	0.306	0.316	3.2
9897	.57	.57	0.0	.110	.108	1.8
10012	.50	.50	.0	.20	.20	0.0
10046	.52	.53	1.9	.050	.050	.0
10047	.63	.64	1.6	.055	.054	1.8
10049	.20	.21	5.0	.147	.148	0.7
10053	2.31	2.35	1.7	.187	.193	3.2
10054	1.47	1.44	2.1	.153	.150	2.0
10109	1.25	1.28	2.4	.127	.128	0.8
10110	1.08	1.11	2.7	.053	.053	.0
10187	0.54	0.53	1.9	.024	.023	4.1
10259	.28	.28	0.0	.79	.79	0.0
10260	.22	.21	5.0	.84	.81	3.7
10261	.96	.94	2.1	.039	.039	0.0
10346	.69	.74	6.9	.35	.38	8.3
10347	.235	.25	6.2	1.46	1.48	1.3
10348	.80	.76	5.0	0.035	0.032	9.1
10389	.73	.71	2.8	.070	.067	4.4
10428	.30	.30	0.0	.21	.22	4.5
10429	.42	.42	.0	.23	.24	4.2
10430	.28	.27	3.6	.182	.188	3.2
10431	.32	.32	0.0	.161	.162	0.6
10434	.29	.30	3.3	.25	.26	3.8

TABLE 7.—*Deviations of results from accepted values on periodic check runs of standard samples*

Element	Range of concentrations	Total runs	Deviation from accepted value				
			0 to 2 percent	2 to 4 percent	4 to 6 percent	6 to 10 percent	10 to 14 percent
	Percent						
Copper	0.29 to 0.94	23	15	5	3	0	0
Lead	.01 to .17	24	12	7	4	1	0
Iron	.015 to .07	28	9	6	4	6	3

The accuracy of the results depends not only on the precision of the spectrographic determinations but on the care in sampling the tin and on the reliability of the reference standards. The precision has been discussed. Serious sampling errors are probably avoided in the methods employed in preparing the samples. The reliability of the reference standards is perhaps best indicated by the agreement of the measurements with the analytical curves (table 4), where the average deviations were shown to be about ±2.5 percent. It is believed that the deviation of the routine single determinations from the actual concentrations is, in general, less than 5 percent and may be reduced to 2 percent under favorable conditions.

2. ADVANTAGES AND LIMITATIONS OF THE METHOD

The spectrographic method of analysis described in this paper offers several advantages over the chemical analysis. Of primary importance is the gain in speed; other advantages lie in the certainty of detection of metallic impurities, the attainment of higher accuracy for low concentrations, the ease of carrying out the analysis, and the possibility of analyzing very small samples. The following discussion of these points is of interest in evaluating the method.

The time required by one observer for the spectrographic analysis of six samples of fusible plugs, where four determinations are usually required on each sample, is a total of 2 hours. This includes preparation of electrodes, photography, photometry, and determination of concentrations from analytical curves. The average time per determination is 5 minutes. The wet chemical determination of the same elements in the six samples requires 2 days after the sample has been milled in the shop. The time required for the spectrographic analysis of other types of tin samples, such as pig tin, is not much longer than that for fusible plugs. The equivalent, complete, wet chemical analysis for 8 or 10 elements would require at least 4 days.

The spectrographic routine method permits a check on the presence of 10 elements, thus eliminating the danger that important metallic impurities will be overlooked. The chemical analysis, on the other hand, may be limited by the time available to the determination of a few impurities most likely to occur. For example, the routine chemical analysis of fusible plugs covers the determination of copper, lead, iron, and zinc; however, four fusible plugs recently subjected to spectrographic analysis each contained 0.2 percent of antimony, which was readily detected and determined. This impurity, which raised the value for the total impurity above the permissible limit of the specification, would probably not have been detected chemically by the short routine procedure used.

The accuracy of the spectrographic method compares favorably with that of the routine chemical method in the region of 1 percent of impurity and exceeds it below 0.1 percent, where the errors of separations and weighings become appreciable. The spectrographic method consists in a series of operations with physical instruments and involves a minimum of reliance on the observer's judgment. Therefore, after the method has been established and the instruments are functioning properly, comparable results might be expected, and, in fact, have been observed for measurements made by different observers having varying degrees of experience.

This method involves the alteration of only the small surface area of the electrodes during sparking; consequently, it may be adapted to studies of inhomogeneity of specimens as well as to the analysis of small samples. In the latter case, millings or drillings can be pressed into a thin layer on the end of each of two tin rods to form electrodes for analysis.

Limitations of the method may lie in the requirements for complex equipment, an insufficient sensitivity for certain nonmetallic elements, and the possibility of errors caused by segregation of impurities. The equipment, of course, can be employed for the analysis of a wide variety of metals and alloys under conditions similar to those outlined for the analysis of tin. It must be recognized that success of the step-sector method rests on the uniform illumination of the sector and the alinement of the spectrograph slit jaws. An occasional check of the line intensity over the effective slit length, with the sector open, will demonstrate the reliability of the adjustments. If a sensitivity of test higher than that provided by the procedure described is desired, two possibilities are open. First, the time of exposure of the spark may be increased, preferably by photographing a composite of two or more 1-minute exposures of the same electrodes, machined between exposures. Second, for the elements arsenic, antimony, cadmium, and zinc, recourse may be had to more sensitive spectral lines, some of which lie in the lower ultraviolet region of the spectrum. Segregation in tin samples, which can be studied by this method, as mentioned above, is a possible source of error when information on the average composition of a sample is desired. By taking the precautions of proper sampling outlined earlier in the paper, the danger of serious error from this source should be eliminated.

The spectrographic method, as described, has been adopted at the National Bureau of Standards for the routine analysis of commercial tin samples submitted for test under the various governmental specifications.

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