THE EMISSION SPECTRA OF LEAD-TELLURIUM ALLOYS

Thesis for the Degree of M. S.

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Spectrum analysis

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BY

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A THESIS

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The Emission Spectra of Lead-Tellurium Alloys

Introduction:

Recently it has been shown that an alloy of lead and a very small amount of tellurium gives a metal product which is very resistant to oxidation. Whether the alloy is to be exposed to the natural forces of corrosion or to the severe action of an anodic potential, it withstands chemical action better than pure lead.

The amount of Tellurium present to give the alloy this property of resistance to corrosion is usually less than one per cent. A chemical method for the determination of small quantities of tellurium in its alloy with lead has been developed by W. J. Brown (Ind. Eng. Chem. (Ann. Ed.) 6 pg. 428, 1934) and the procedure is very long. Since the spectra of Tellurium is rather simple and its most persistant lines, namely, of wave lengths of 2383.27 I. A. and 2385.78 I. A. are not interfered with by any lead lines it was decided that the intensity of these lines could be made the basis of a new method for the determination of Tellurium in its alloys with lead. This physical method should be faster and as accurate as the methods of wet chemical analysis.

The spectrograph has long been successfully used for the qualitative analysis of many elements. In quantitative work it is especially used for estimations of traces and minor constituents too small for satisfactory chemical analysis; for rapid estimations of elements present in small amounts which would require slow and complicated methods of analysis; for determination of the approximate composition of materials when amounts available are too small for chemical analysis. The problem of estimating the amount of Te in Tellurium-Lead Alloys in this laboratory was based upon the fact that as the concentration of a constituent is increased the intensity of the light from that constituent is increased. The estimations were to be based upon the relation between the intensities of the Tellurium spectral lines in the sample with the intensities of the corresponding lines of the spectrum produced from standard samples of known composition.

Many applications of the spectograph are suggested by Walter Gerlach in "Foundations and Methods of Chemical Analysis By the Emission Spectrum". Although his work is almost entirely confined to the spark method of excitations, the principles involved cover a very wide field.

Apparatus and Materials:

The medium quartz spectrograph, an instrument manufactured by the Bausch and Lomb Co. was used in this work. The instrument used must have sufficient resolving power and dispersion to separate clearly the lines of the constituent sought from the lines of the other elements present. At 2400 A the dispersion is about 6 A per millimeter. The total dispersion of 7,000 A-2,100 A may be photographed on one ten inch plate.

The instrument must be equipped with an illuminating system to give satisfactory results. A Bausch and Lomb electrode attachment with electrode adjustments which move each holder independently. in a vertical direction, and together horizontally by means of a lateral base adjustment was used in this work. The electrode stand was mounted on the optical bench.

The lenses may be used for condensing the emission spectra of the source. The focussing lens requires a spherical lens of approximately 4cm. diameter. It is used to focus the image of the hot electrode tips just above and below the slit opening respectively. The light between these images may be condensed with a cylindrical lens which will concentrate the light passing through the slit. (Research with the spectra of the Lead-Tellurium alloys was carried out without the use of either lens.)

Mounted on the optical bench is a motor driven sector diaphragm which when in operation will eliminate from 50--100% of the light, thus permitting longer exposures at lower intensities.

The electrodes used were regraphitized Acheson rods.

The photographic materials and apparatus used were Eastman 33 commercial plates and D-1 tray developer and acid hypo solution.

Special reading lens and lantern, Bausch and Lomb instruments, were used for observation plates. A special vernier comparator made by the Bellingham and Stanley Ltd., London, was used for qualitative work in determining wave lengths.

The timing device used was a standard stop watch. However, automatic devices are available for special work.

Methods:

A-Standard Limits (C. C. Nitchie, Ind, Eng. Chem. (Ann. Ed.) 1. pg. 1, 1929).

The emission spectra of an arc is characteristic qualitatively and quantitatively of substance being arced, and through repetition of a set of workable conditions for each exposure a spectrogram on a photographic plate may be produced that will show visually the relative intensities of characteristic lines of the elements to be estimated. Such conditions of arcing and exposing must be guaranteed to give a total exposure of a definite quantitative amount of the alloy during a definite arcing time. For a given range of intensities the plate is sensitive to the total amount of dispersed light striking it and the difference in the "blackening" or intensity of the lines produced will be relative to the percent of the element to be estimated.

The above principle was used to determine the relative amounts of Te in Pb-Te alloys ranging between .005% to .5% Te. Standard samples or alloys of the same composition as the alloys to be analyzed were prepared. Two methods were used to produce an emission spectra of a quantitative sample, but the plates obtained by both methods were interpreted visually by the same procedure. Exposures of standards containing various increasing percents of Te were made on a spectrographic plate arranged so that a similar plate made under the same conditions as the first can be superimposed upon it. A series of gradations for a preliminary plate may be shown by use of concentrations of multiples of two as (.1%, .05, .025, .0125% etc.). From the standard plate we can estimate the approximate range in which the correct percent will be found, by making a second plate showing several consistent exposures of the unknown. This plate may be used as the preliminary plate for the analysis of several alloys. After estimating the approximate percent from the standard plate a third plate must be made using a series of standards of five or more in a decreasing or an increasing order of concentration with alternate spectra of the samples of the unknown. From this plate the technician observing the plate will find it possible to estimate the percent Te from the lines of a standard equal to or more nearly equal to those of the unknown than to any of the other standards. The percent may be estimated or given as the same as one of the standards if it appears to be of the same percent. Where more accuracy than (plus or minus) 5% of the actual quantity present is required another plate using standards in that range having a smaller differential in the percent. This plate will enable the technician to be more accurate in the estimation of the percent of the Te present.

Two methods were used to produce the spectra from the arc. Carbon electrodes were selected and solutions of the standards were used to impregnate the lower electrode for each exposure with a definite volume of the standard solutions. After evaporation the electrode was dried and used in the arc. The impregnated salt thus burned out completely and gave a quantitative exposure.

The second method made use of the alloy directly. A sample of the unknown or standards of twenty milligrams were introduced into the crater of the lower electrode. The carbons arced and the sample burned out completely during the necessary time due to the high temperature of the arc giving a quantitative exposure comparable to the first method using solutions. These two methods are not interchangeable in one analysis but either has been found satisfactory under the proper conditions for separate analysis.

Many methods for carrying out a spectrographic analysis are described in literature. The features which are characteristic of various methods involve the form of the sample, manner of excitation, type of spectrograph, and manner and methods of interpret~~t~~ing the sample spectra and estimating the constituent sought. It was not the purpose of this discourse to describe the several methods used in other laboratories, but it was necessary to investigate various methods in order to develop a method to meet the requirements of this problem.

Procedure Involved:

The excitation, arcing, including volts, amperes and time required, focusing of the spectrograph, preparation of electrodes, determination of the correct amount of light, exposure of the photographic plate, and development of the plate are in general the conditions involved which must be treated with a technique that may be duplicated with each exposure.

The excitation for the arc is supplied by a 12 ampere 300 volt motor generator and by means of the voltmeter and ammeter, the carbon rheostat may be adjusted to give 6 amp~~h~~eres and approximately 35 volts. The time that the exposure requires is the first four minutes of arcing which under proper conditions permits the complete volitilization of the sample. The spectrograph should be previously focused to the correct alignment using copper electrodes, the slit width of four corresponding to approximately .04mm. and a diaphragm giving a slit height of approximately 3mm. The total amount of light that would strike the plate from a four minute exposure must be reduced to approximately 20% to prevent over-exposure.

Two procedures may be used in the preparation of the electrodes. The high grade graphite rods to be used as electrodes shoul be about two inches in length. The lower electrode, positive, is prepared with a crater of approximate dimensions of 3 x 6 mm. and the upper electrode is filed wedge-shaped. The lower electrodes to be used are impregnated by filling each crater with 0.1 cc of solutions containing the samples or standard alloys, the concentration of the solutions being such that o.1 cc contained 12.5 mgr. of the alloy. A diluteenitric acid solution should be used and various standards made by diluting with proper solutions of Te-free lead made up to the same concentration. These filled electrodes are placed in an electric furnace for thirty to forty minutes during which time complete evaporation is assured, leaving the salt impregnated in the pores of the carbon crater. These electrodes are now ready for arcing and exposures may be made in the order which may be demanded. For example, if it is to be a plate of standards for reference, the exposures would be made in pairs and each pair sufficient distance from the next to allow insertion of a sample spectra from another plate. However, if it is to be a typical analysis, we would first have a standard of a higher percent tellurium than expected followed by the sample, then another standard lower than the first, and finally another spectra of the sample followed by another standard approximately equal to the sample etc., until the standards range above and below the expected analysis. All of these exposures should appear very close to each other for observation purposes.

A second method may be used instead of the solutions to impregnate electrodes. The samples may be cut from the alloy and weighed out accurately. In this work twenty milligram pieces were used in the crater of the carbon electrode. The craters for this procedure arc about 2 mm. in diameter and about 4 mm. deep, the procedure thereafter being the same as used above. In general, two analyses on one plate are a maximum as the amount of time saved would not justify the fact that the plate may be lost through fogging or some accident which would be a heavy loss if it represented too much work.

The plates are developed with Eastman D-1 tray developer for seven minutes at a temperature of about 18° C. After developing, the plates should be rinsed in water and then fixed in Eastman acid hypo for twenty minutes or approximately twice the required time for clearing. After washing in running water the plates should be swabbed with cotton and allowed to dry.

The technical interpretation of the plate depends upon the procedure followed. In general, a relative comparison of intensities is made until the percent may be estimated. If two observers analyze the plate independently and report results which check satisfactorily for the specifications required, the analysis may be accepted. If results are not positive, another plate must be made for proper results. Investigations of the development of this procedure and several typical analyses will be discussed subsequently.

Discussion of Investigations and Results:

Selection of Spectral Lines:

A primary requirement for the estimation of Te in lead spectra is that the lines used in comparing the plate be of such intensity as will vary directly as the amount of Te in the sample. These lines must be of a grayish intensity which are on a straight line portion of the density-exposure curve for the photographic plates used. It will be observed that all lines in the same spectrum characteristic of Te are not of the intensity which makes it possible to work in various ranges of percent concentration. However, it was fount that only a few lines were available for comparison for concentration lower than 0.1% Te. These are also satisfactory for concentrations up to 1% as the relative intensity remains the same if the total amount of light is decreased. The following was found to be representative of the lines selected in this work:

Tellurium lines:	Range in % Te	arc- I. A.
	1. -.0005%	2385.78 2383.27
	1. -.1%	2265.52 2259.02 2255.50

Several other lines may be used if the technique and the type of equipment make it possible.

Sensitivity Limits and Preparation of Standards:

Using the solution method of introducing a sample into the electrode, after complete volatilization on further increase in density of the spectral lines will occur and the carbon spectrum is not particularly harmful for comparison of lines having a wave length less than 3,000 angstroms. The amount of the sample introduced definitely limits the radiations of a certain constituent. The limit of detection depends upon the amount of the sample which can be used in the crater of the electrode for a definite condition of excitation and spectrography. Using .1cc containing 12.5 milligrams of alloy the limiting percent of tellurium that could be detected in the lead means that only .0000000625 grams of the sample was tellurium. With the technique used in this work only a few of the millions of light waves emitted pass through the slit and eventually strike the plate. If dependable results are desired as low as this limiting sensitivity, larger samples must be introduced and more light must be employed by means of reflecting minor or focusing and condensing lenses. Figure 1 represents a 12.5 mg. sample and figure 2 a 25 mg. sample of the same alloy prepared by the solution technique. In figures 1 and 2 the plates represent exposures of 15 minute intervals of two samples being arced continuously. By close observation, the Te lines of the larger sample show greater intensity and persist 15 to 30 seconds longer than those of the 12.5 mg. sample. The persistancy of the second is not twice that of the first but use of this technique in studying plates seems to indicate that a log-function exists between line persistancies of low percent standards Te-Pb alloys. However, size of samples

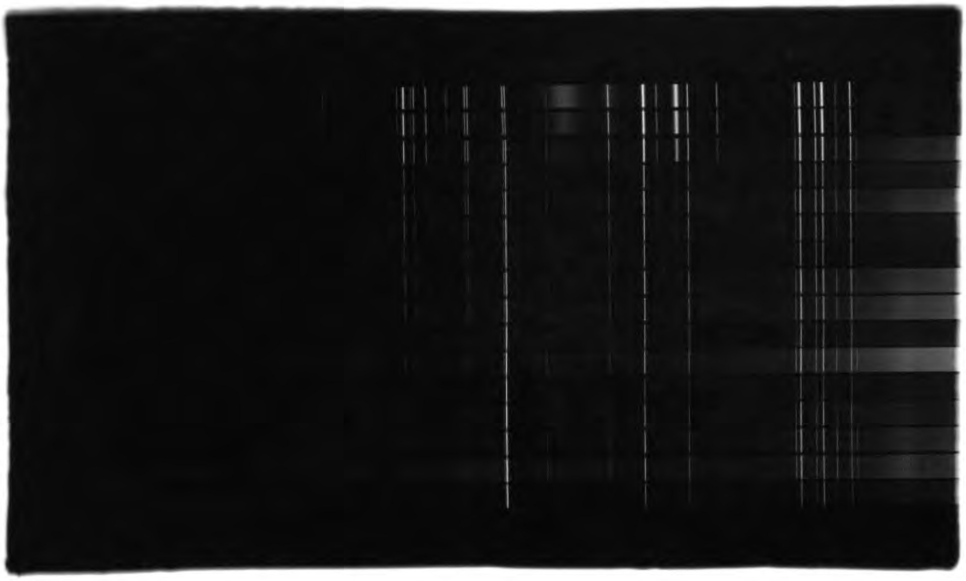

Fig. 1

Pb-Te alloy 0.0187% Te 12.5 mg. solution sample

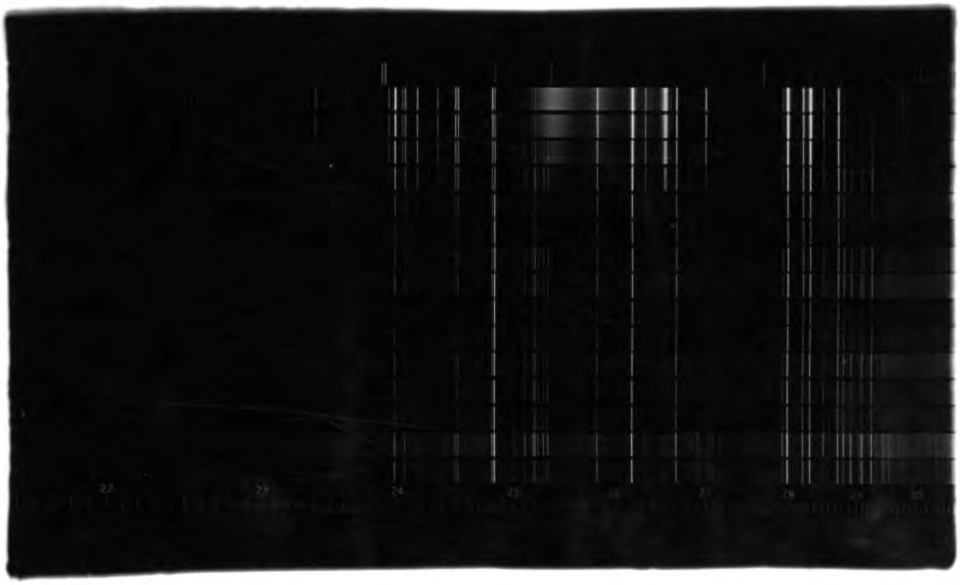

Fig. 2

Pb-Te alloy 0.0187% Te 25 mg. solution sample is sometimes limited by chemical properties. Due to the solubilities of Pb and Te nitric acid was found to be the only suitable solvent and 125. grams metal per liter a convenient concentration. Solution B of pure lead in dilute nitric acid and solution A having a concentration of 247.5 grams pure lead in two liters solution also containing a concentration of 2.5 grams Te giving a 1% solution. Solutions of same concentration may be obtained by diluting proper volumes of A with B. Solutions were prepared as follows:

.5% Te	Solution	C	(100 cc A	plus	100 cc B)
.25% Te	"	F	100 cc C	"	100 cc B
.125% Te	"	I	50 cc F	"	50 cc B
.100% Te	"	J	10 cc A	"	90 cc B
.05% Te	"	M	50 cc J	"	50 cc B
.025% Te	"	P	50 cc M	"	50 cc B
.0125% Te	"	R	20 cc P	"	20 cc B
.0050% Te	"	S	20 cc R	"	30 cc B
.0005% Te	"	T	10 cc S	"	90 cc B

Intermediate standards were prepared as needed by using proportional amounts of above standards.

Preparation of Samples: Solution Technique:

The total amount of a sample consumed by an exposure is very small and could not be selected as representing the entire sample. In general, a large sample may be used such as 12.5 grams dissolved in nitric acid and the solution adjusted to 100 cc which would give the desired concentration. The sample solutions are then handled with the same technique as applied to the standard solutions.

In cases where the solution technique does not provied the sensitivity using .1 cc of the standards, larger aliquots may be used, but above .3 cc it is impractical. If the larger sample introduced into the electrode fails for the sensitivity of the lower percents of Te used, a technique is resorted to where a greater amount of the sample is added to the electrode. For this purpose, the "metallic sample technique" was used.

Metallic Sample Technique and Preparation of Standards and Samples

First, the standard alloys were made up accurately with a homogeneous concentration of Te. This required special technique and equipment. Definite weights of pure Te and pure Pb were weighed out to give desired alloys. Each alloy must be made in the absence of oxygen to prevent oxydation of the surface. The vessel arrangement should be such that the lead would melt first and then dissolve the Te. It is held at the melting point temperature for several hours to assure complete homogeneity. Alloys of Pb-Te of higher percents can be successfully cast in clay crucibles, the surface being covered with carbon to prevent oxidation.

From these metallic standards any size sample required to give the senstivity necessary may be used within workable conditions that may be duplicated.

In carrying out the actual spectrography the procedure will be entirely analogous to the solution technique. A longer exposure time will be required for arcing of a metallic sample and therefore as small a sample as practical must be used. Care must be taken to assure complete volatilization of the sample. The craters of the electrode must not be too deep so that before the complete exposure time has elapsed the remaining bead of the sample will be directly in the arc with the upper electrode which will completely volatilize it.

Time Required for Volatilization:

A study of the time required for the volatilization of the sample, the volatilization time of the Te, and the percent of light necessary to give a line of satisfactory intensity for comparison to other concentrations, made it necessary to develop an original procedure in this laboratory to simplify as much as possible the work required. An electrode was prepared by the metallic sample technique previously described and a spectrographic plate made of its spectrum in continuous exposures of fifteen second intervals, for five or six minutes. Referring to figure 3, it is immediately apparent that fourteen intervals of 15 seconds were required to volatilize the sample.

Referring to figure 4, it is obvious that fourteen intervals of continuous exposure were again necessary. Figure 3 represents a twenty milligram sample of .126% Te. By observing the print, it is evident that the first 15-30 seconds cannot be relied upon for a quantitative exposure as the electrodes must become hot enough to volatilize the sample. Referring to the Te lines of figures 3 and 4, we see that the tellurium is volatilized after seven and nine intervals of fifteen seconds respectively. The time required for the exposure of a sample of this size on this spectrum would be from 210 to 240 seconds if complete volatilization is desired. However, approximately 150 seconds would be sufficient to burn out the tellurium under these conditions of excitation. If the total emission of these exposures was made on one spectrum, obviously the plate would be too dark for observation. On close examination of the Te lines we see that

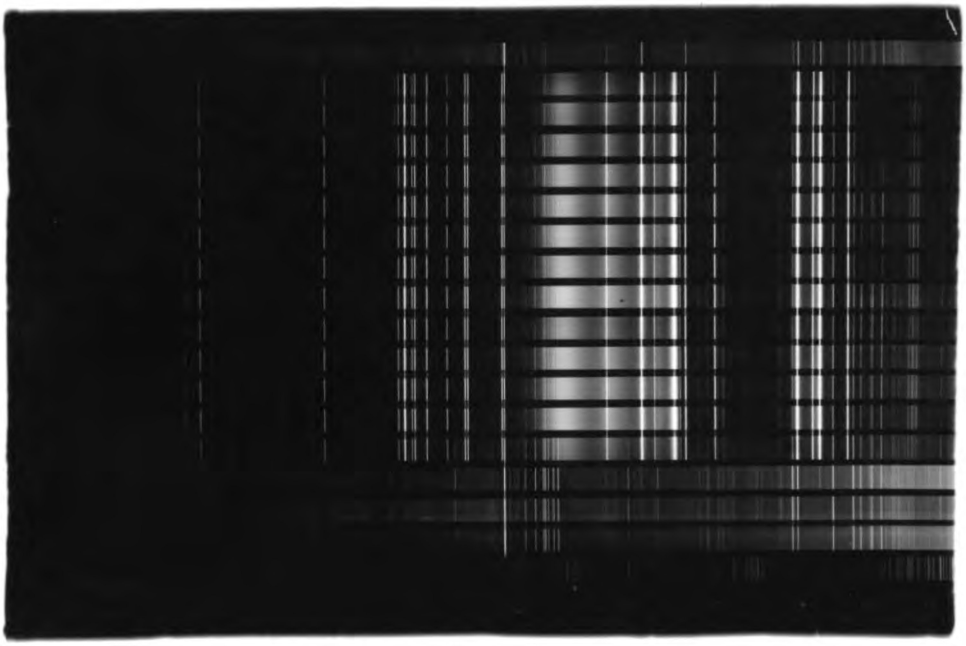

Fig. 3

Pb-Te alloy 0.11% Te Metal sample

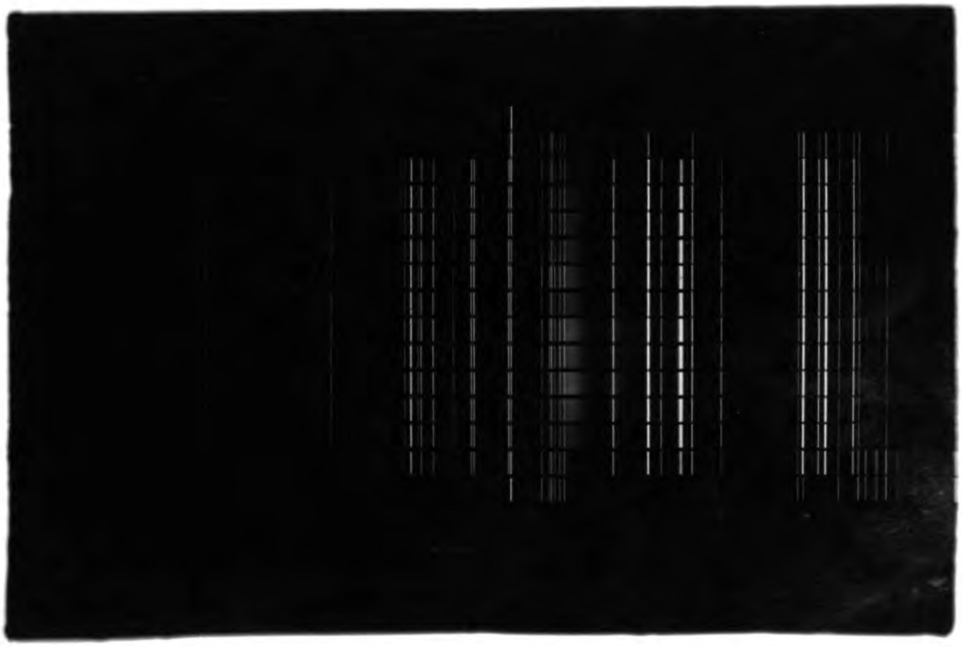

Fig. 4

Pb-Te alloy 0.126% Te Metal sample

about five sets are of the intensity desired. If we use about twenty percent of the total light we will obtain lines proportionally sensitive to the Te concentration. This we will have exposed the plate forty eight seconds but the plate shows the lines in the ultra-violet very clearly. It was found that results could be duplicated with less irregularity by volatilizing the entire sample, and consequently four minutes became standard in this work. It is interesting to note that as the lead lines disappear the impurities of the carbon come out very brightly. In figures 1 and 2 the first spectra is that of Te metal. The last spectra is that of iron for determining wave lengths.

Standard Reference Plates:

The comparison method for determining the amount of the constituent present requires a reference plate of a maximum range of standards. These plates must consist of exposures made in an increasing or decreasing order of concentration of the element under analysis. Each set of conditions used in the analysis requires an individual standard plate having been prepared under duplicate conditions. In figures 5 and 6 standard plates are represented for "solution technique" and "metallic sample technique" respectively. The Te. lines show a gradual decrease in intensity. The negative plate is depended upon for analysis and the print may or may not be able to make this gradation series obvious. This plate will be used later in a typical analysis. Figure 6 shows a standard plate used for reference in an analysis using the metallic sample technique. An analysis will also be illustrated by this method.

Fig. 5

Pb-Te standard alloys   Solution standards

Fig. 6

Pb-Te standard alloys   Metal Samples

Analysis of Two Alloys by the Solution Technique:

Two alloys for analysis were selected from a group of Pb-Te alloys known to be of low concentration of Te. Each alloy was sampled and treated as outlined for use in a solution having a metallic concentration of 12.5 mg. per .1 cc. In a manner similar to the spectrography of that used in the preparation of the standard plate for this method, five exposures were made successively of each of these two samples. The Plate was developed by the same photographic technique as previously used. Referring to Fig. 7 we first may observe that Te. lines of equal intensity appear for each sample which should assure the operator of reliable results; secondly by comparing the negative plate of Fig. 7 with the plate of Fig. 5, we can estimate the approximate percent Te. of both alloys. It was found alloy #1 was between .1% and .30% Te, and alloy #2 was between .025% and .10%. From this information it was advisable to compare the line intensities in question to closer standards on the same photographic plate to eliminate any variation in the sensitivity or plate development. Referring to Fig. 8, standards ranging through the estimated percents in a decreasing order were spectrographed with alternate samples for analysis. The plate may or may not be developed with the same technique as a standard plate as small variations occuring will affect all lines accordingly. Observations of this plate if satisfactory will enable one to estimate the percent unknown in the alloys. Reports of two observers were checked and agreed very closely to the estimations made by the author. If the percents reported

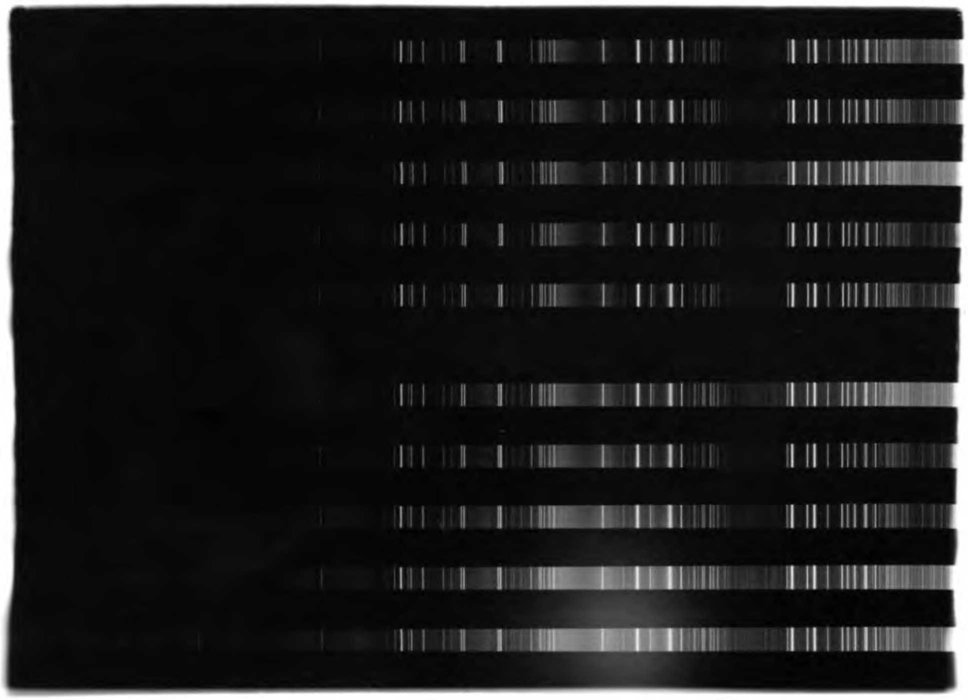

Fig. 7

Preliminary analysis of alloys 1 & 2. Solutions

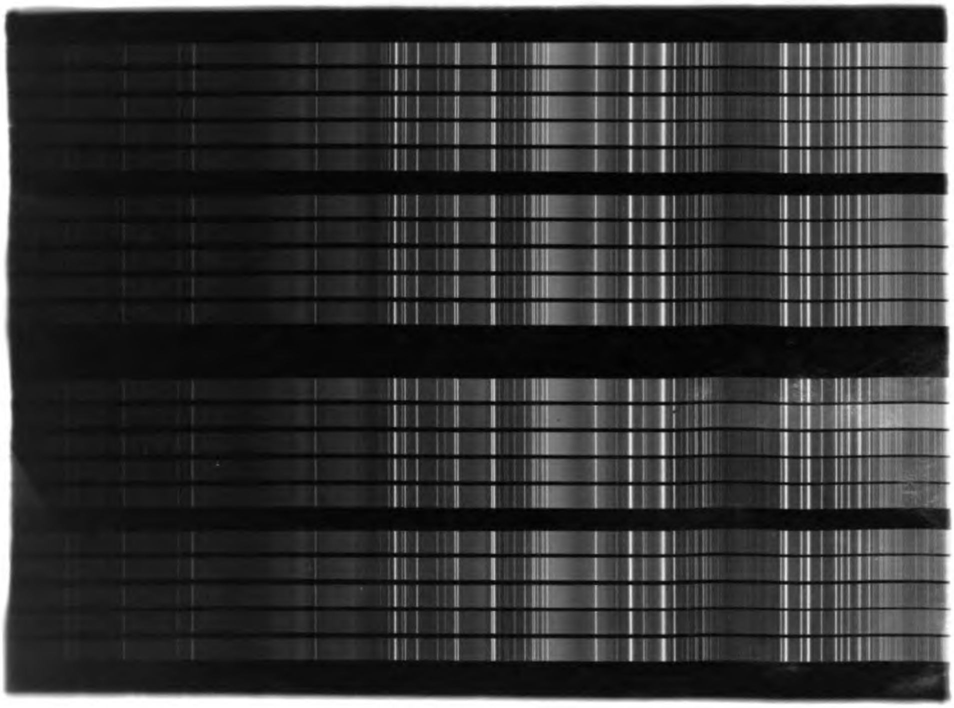

Fig. 8

Final analysis of alloys 1 & 2. Solutions.

by two workers should not check within the required limits of accuracy, another plate must be made that will yield acceptable results.

Using alloy #2 and selecting another unknown #3, an analysis was made of each, applying the metallic sample technique. Alloy #3 was known to be between .07--.09% Te. Using this information, a final plate could be made at once. As shown by figure 9, the standards available in the respective ranges were spectrographed with alternate samples of the unknown applying the conditions previously outlined. Observations of the negative of fig. 9 would show alloy number 2 to be very nearly .05% Te. and alloy number 3 to be .08% Te.

Estimations of Te. in alloy #2 of .05% indicates the reliability of the metallic sample technique to be comparable to the solution technique.

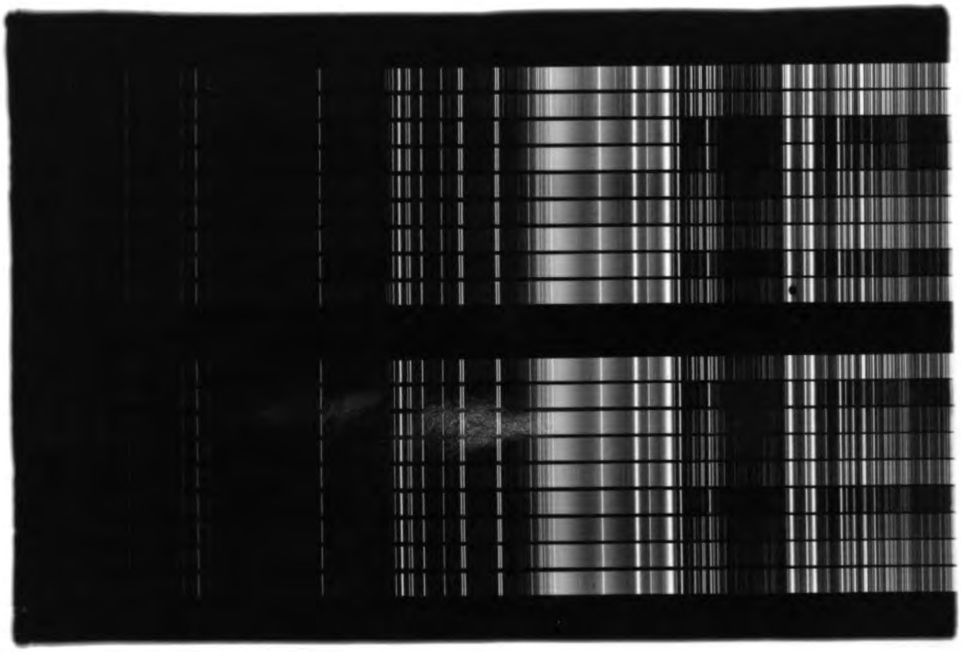

Fig. 9

Final analysis of Pb-Te alloys # 2 & 3. Metal samples

Special Notes

Selection of Carbons:

Graphite rods produced by six companies were available for use. In order to select an electrode for spectrographic use it must be studied from the point of view of the use to which it is to be employed. The carbons must be of certain limits in diameter to withstand arcing conditions. However, the important point to consider is the impurities and the possibility of their spectral lines interfering with the characteristic lines of the spectra being studied. Fig. 10 shows the spectra of six carbons for long and short exposures. The carbons which would be used were selected first from the spectra standpoint and second from their cost and the supply on hand. Acheson graphite rods were selected and found to be satisfactory after a positive qualitative analysis for Mg, Cu, Fe, Cr, Ca, B, V, Si, Mn, Fe, Al and Ti. Impurities found present wer Mg, Mn, Fe, Cu, Al, Ca, Ti, and V. However, the only interfering line was Fe at 2382.04 which is very close to a characteristic Te. line at 2383.27. Some investigations of the use of a photomicrometer for measuring differences in line intensities were made and it was evident at once that interfering lines were marked disadvantage. Referring to fig. 11, the print illustrates the analysis of a carbon for impurities.

Qualitative Analysis of a Pb-Te Alloy to be Analyzed for Te:

In order to make a satisfactory estimation of an element present by the method of comparison it is necessary that the

Fig. 10

Spectra of six commercial graphite electrodes

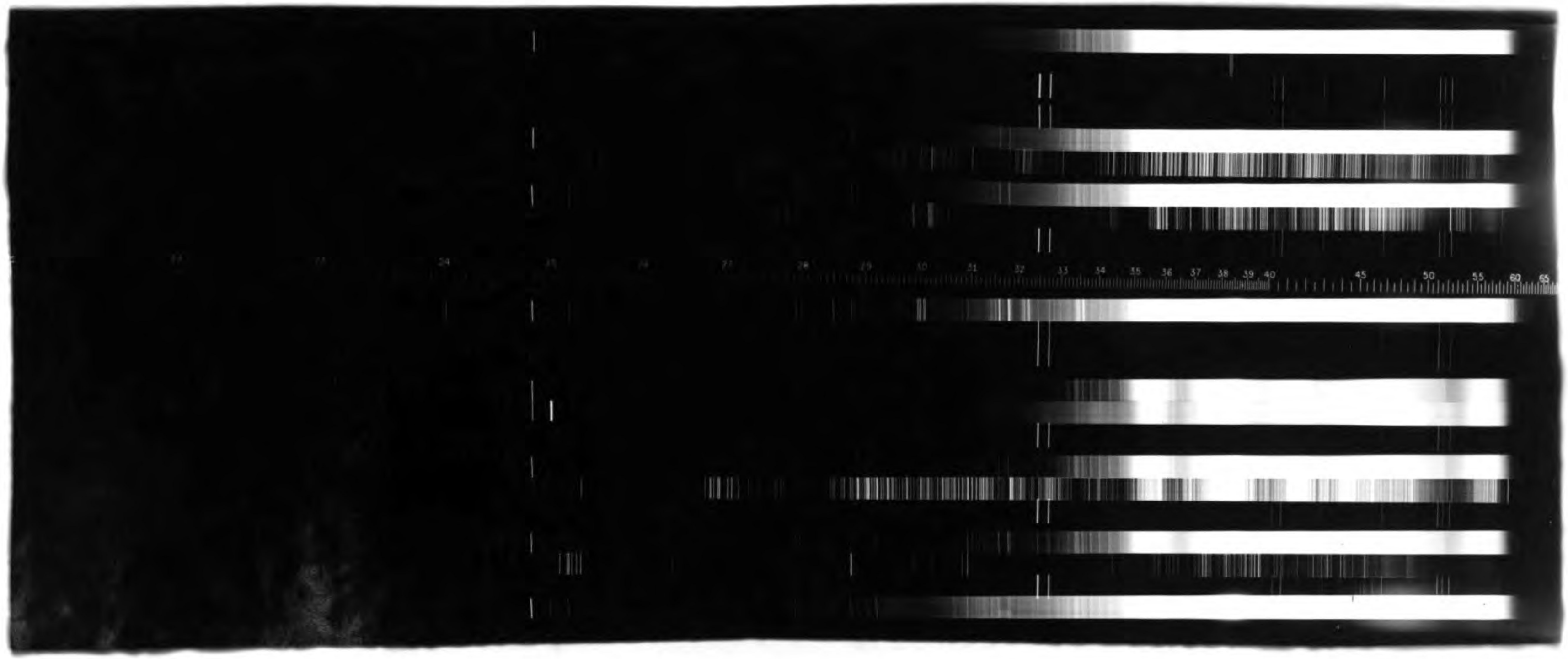

Fig. 11

Qualitative analysis of Acheson Graphite Electrodes standards not only contain the base metal and the element in question but also the same concentration of almost any other element present whether as a part of the alloy or an impurity of it. This is due to the effect of certain elements when present holding back the intensity of other lines which may be the lines of importance. If very small impurities are known not to interfere than they may be neglected. In figures 12 and 13 is represented the analysis of the Pb-Te alloys for Cu, Ag, Mg, and traces of Fe, Cd, As, and Si were found to be present, and the difficulty with which their characteristic lines appear, indicate no interference with the tellurium lines studied.

Selection of Lead for Base Metals:

The purest lead standards were selected because of their more general use to any of the alloys impure or pure. In figure 14 is shown a comparison of three very pure leads used in laboratories for such work. These leads were compared at various time exposures and current densities of arcing, and the Central Scientific Co's silver free test lead was selected for use as a base metal in the alloys and solutions.

Samples of Te. Above the Range of Spectrograph:

Such samples as may be too high in concentration of Te. for the spectrograph or standard solutions available may be diluted with a solution of pure base metal in such a proportion as to reduce the Te. concentration several times. After analysis this percent may be corrected by the dilution factor. However, such concentrations are generally estimated by wet analysis.

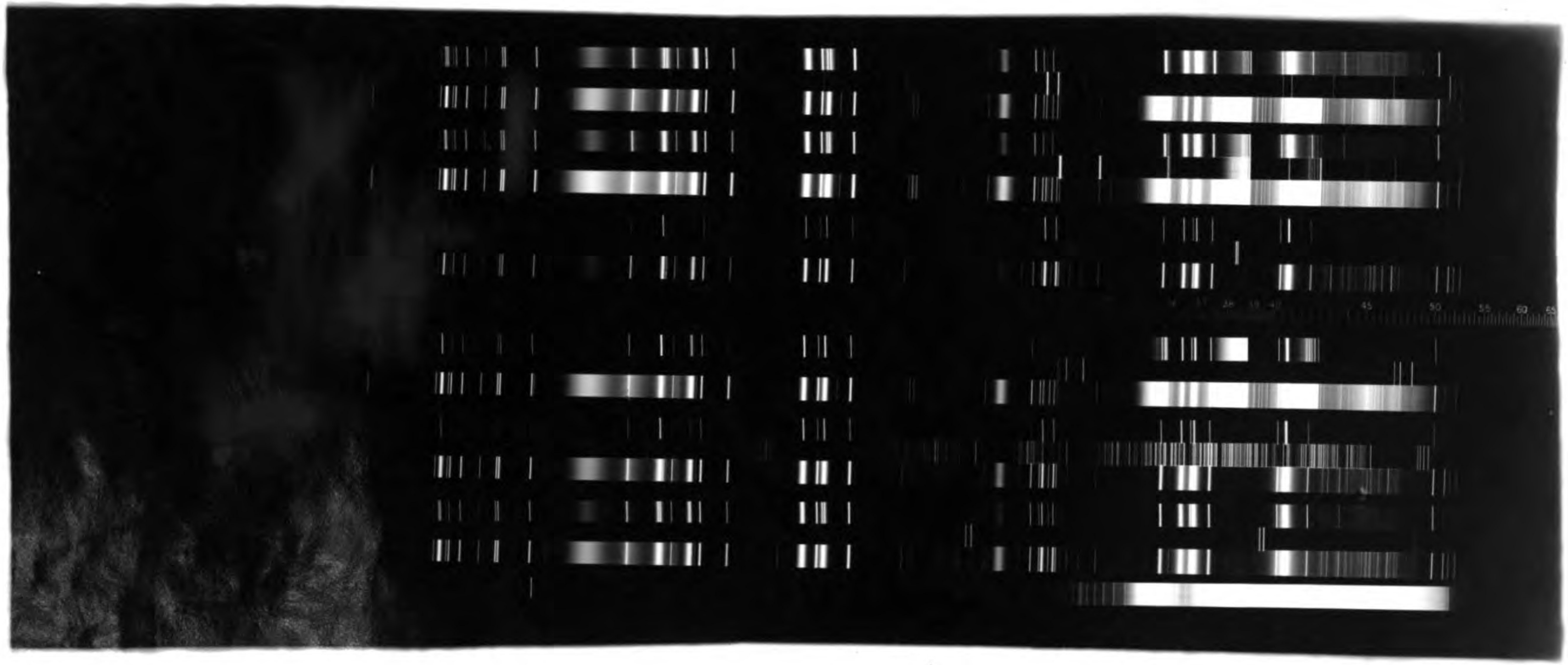

Fig. 12

Qualitative analysis of a Pb-Te alloy for impurities

Cu, Ag, Mg, and Fe present, Zn and Al absent

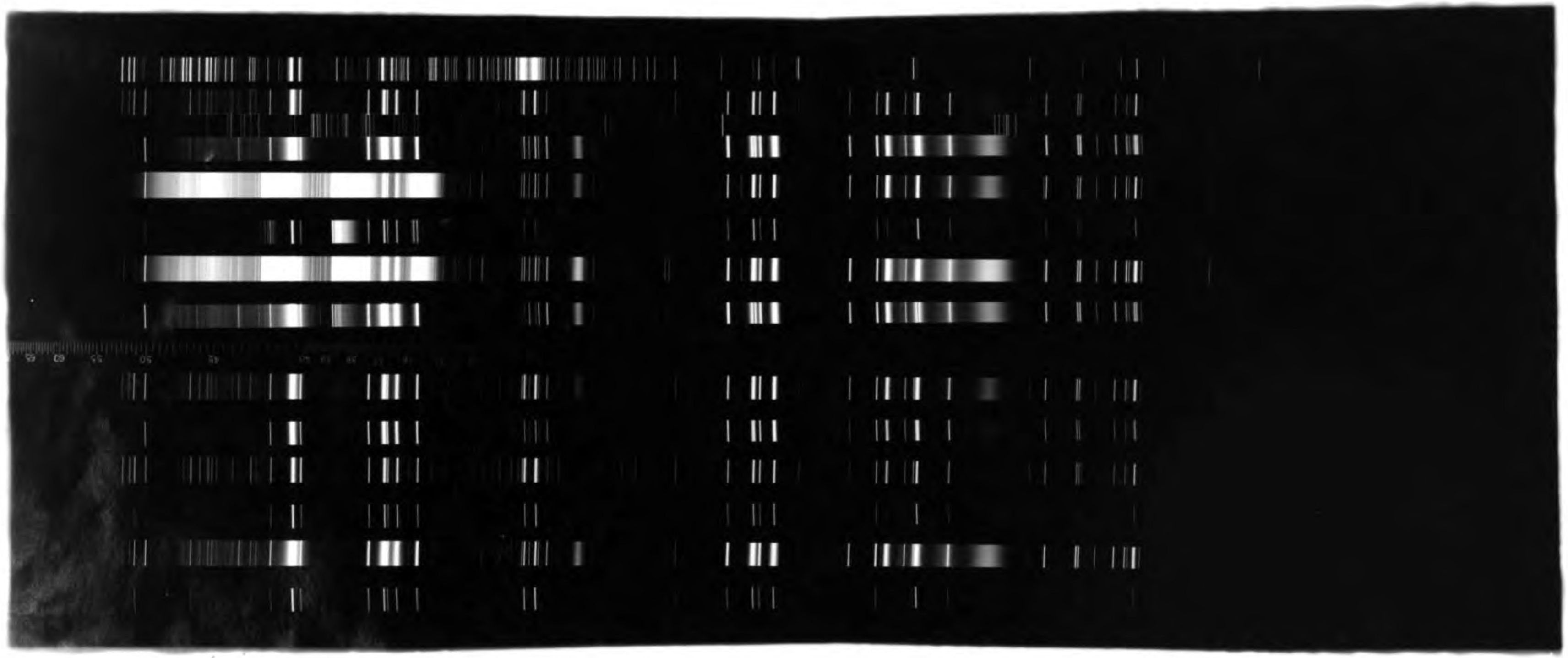

Fig. 13

Qualitative analysis of a Pb-Te alloy for impurities

Cd, As, and Si present in traces; Sb, Bi, and Sn absent

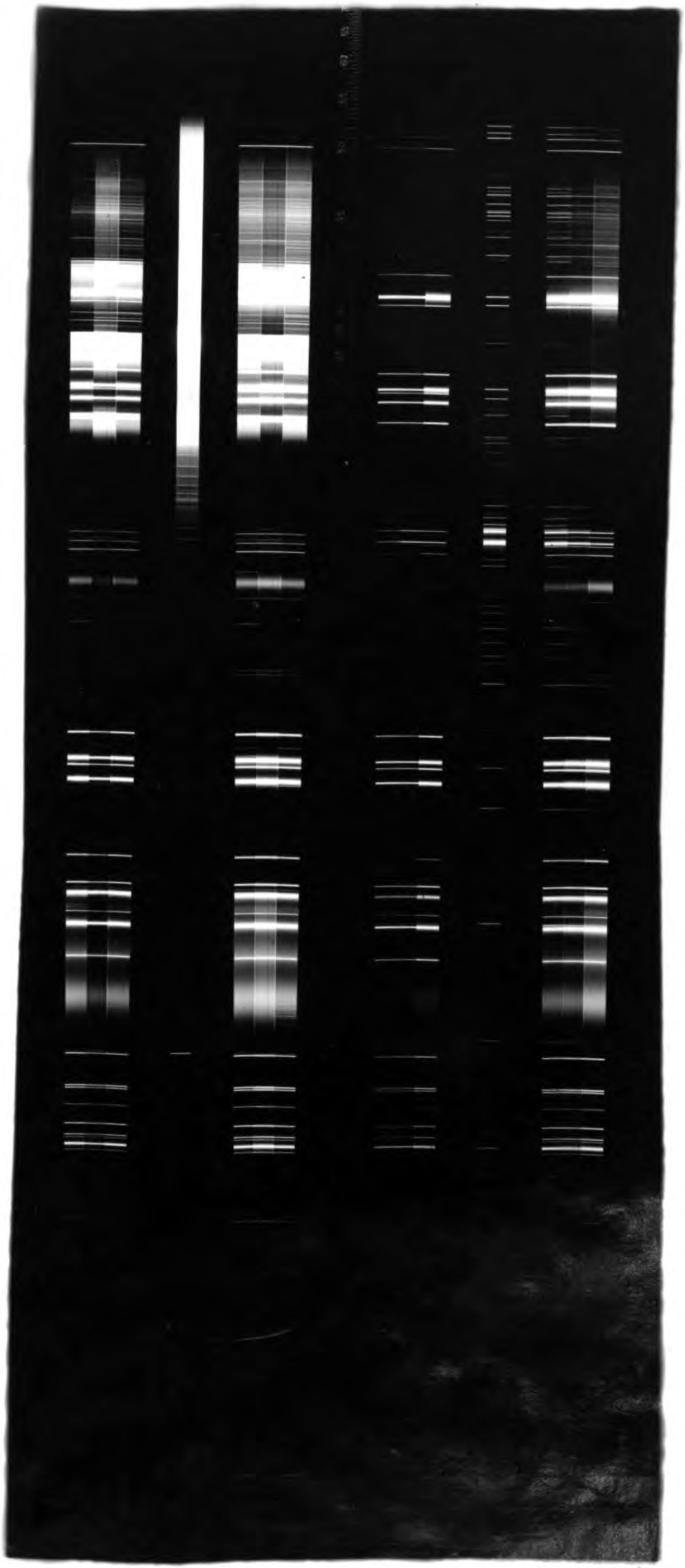

Fig. 14

Qualitative comparison of three Pb supplies for the base metal of standards

Conclusions:

1. The methods pursued and developed in this work may be adapted and expanded to meet the requirements of many problems of a similar nature. The work here developed has employed methods previously used in other laboratories and does not represent an entirely original investigation. However, the technique used shows many changes over the procedures suggested by other workers. Information required from time to time in this work has suggested many research problems which should lead to new spectrographic methods.

2. The method used here for the study of time exposure and intensity of lines employing a continuous burning out spectrum seems qualified as a distinct rapid method of quantitative analysis. Rapid estimations are at once obvious to the eye. Interfering lines may burn out first permitting the examination of others, and other important facts which are only available from a picture of the arc at succeeding intervals of time during the burning out of the sample.

3. The use of the spectrograph in commercial and scientific research laboratories is being adapted to many problems covering a broad field in which physical properties of materials are studied upon the basis of the constituents present. Detection of the impurities or quantitative estimation of minor elements in alloys is a special problem which must be developed in order to meet the demands of modern industry and science.

The emission spectra of lead-tellurium alloys.

May 4 '39 A. Mueller		
May 20 '42 G P Koch		