

A METHOD OF ANALYSIS BY MEANS OF THE SPECTROGRAPH

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A METHOD OF ANALYSIS BY MEANS OF THE SPECTROGRAPH

A spectrographic method is described herein for the quantitative determination of metals present as minor constituents or impurities in alloys, salts, solutions or other materials. Improved methods of measuring photographic blackenings are employed which result in a more accurate evaluation of relative spectral intensities. This is an essential and fundamental part of any spectrographic analytical procedure.

In this investigation the method was used for the determination of several metals present at very low percentages in copper alloys. A new procedure of photographic plate control is demonstrated incorporating internal control without the use of computed ratios of spectral intensities or photographic blackenings. The applicability of the method for the elimination of some undesirable effects of the variable characteristics of the spectrogram such as those arising from the processing technique or photographic materials is emphasized.

The demand for more rapid methods of analysis of substances for impurities or minor constituents has been increasing for some time and for certain classes of materials this need is being met with the spectrograph.

Lockyer, (Lockyer, N., *Trans. Roy. Soc. (London)* 164, II, 479 (1874), an early investigator in this work, noted that the distance a spectral frequency could be observed from the source varied with the amount of the element emitting that frequency. Since then a number of procedures have been introduced for the spectrographic quantitative estimation of elements. These procedures are based on the principle that as the concentration of an element increases the intensity of the light emitted by the spectrum of that element increases. The results of the analysis are obtained by the comparison of these spectral frequencies with the corresponding frequencies in samples of known concentrations. In general, all the methods involved the recording of the spectrum on a photographic plate, giving a series of lines which are images of the slit. Each line corresponds to an individual spectral frequency in the light which entered the slit.

The various methods described in the literature for the spectrographic determination of an element may be differentiated by variations in the form of the sample, means of excitation, type of apparatus used, and the procedure for the utilization of the spectrum. Gerlach (Gerlach, W., *Z. Anorg. Allgem. Chem.* 142, 389 (1925) found that a large error was due to the comparison of the lines of one spectrum to the corresponding lines in another spectrum. He reduced this error in his method of "internal control" by correlating the density of certain selected lines of the major element of the substance being analyzed with the blackening of the line or lines of the element being determined. A set of standard specimens was used to prepare a chart showing the concentration steps at which pairs of lines of the same blackening were found. The analysis was carried out by the inspection of a spectrum of the unknown for such a pair of lines. If a pair of lines of equal blackening was found, the chart was consulted for the concentration. Gerlach used this method in order to reduce the errors encountered in attempting to reproduce spectra.

This visual matching of pairs or the interpolation between steps in a standard series of pairs was soon replaced by more flexible methods. Twyman and Hitchen (Twyman and Hitchen, *Proc. Roy. Soc. (London)* 31, 169 (1930), Nitchie and Standen, (Nitchie and Standen, *Ind. Eng. Chem., Anal. Ed.*, 4, 182 (1932) and other workers used mechanical and optical means of evaluating the relation between photographic blackening and the concentration of the element under test. Blackening-concentration curves were constructed. By standardization of the conditions of exposure and the photographic procedures a concentration was obtained by the evaluation of the blackening on this curve. The photographic variables encountered were such that for more accurate results a series of standard specimens of known concentrations was used on each spectrogram for comparison with the specimens for analysis. Using this procedure the results were obtained by either visual comparison or optical measurements. A blackening-concentration curve for the individual plate may be used for the analysis. By comparison or evaluation of photographic blackenings as functions of the concentrations less accurate results were obtained than by the comparison of spectral intensities with concentration. This was attributed largely to the errors introduced by the variations in the photographic materials and the processing of the spectrogram.

Thomson and Duffendach (*J. Op. Soc. Am.*, 23, 101 (1933) described a method of measuring the relative intensities of spectral lines in which a Hansen (Hansen, G., *Z. Physik*, 29, 356 (1924) "step-diaphragm" was substituted for the slit of a spectrograph and a source of continuous light was used. A series of continuous spectra are produced by one exposure in which, for a given frequency, the intensity of the light varies as the known widths of the openings in the diaphragm. When the blackening values of these continuous spectra are graphed against the corresponding relative intensities a "calibration curve" is produced. This curve may be used to find

the intensities corresponding to the blackening values of the line images of the spectral frequencies on that plate. Hurter and Driffeld (**Hurter and Driffeld, J. Soc. Chem. 9, 455 (1890)**) made a series of investigations of photographic materials and clearly set forth the characteristics of this calibration curve. This curve is sometimes referred to as an H and D curve. Such a curve was made for the calibration of each spectrogram by Duffendach, Wolfe, and Smith (**Duffendach, Wolfe, and Smith, Ind. Eng. Chem., Anal. Ed., 5, 226 (1933)**). From this curve the relative intensities for the spectral frequencies were found. These intensity values are expected to vary as functions of the concentrations. Under proper excitation conditions ratios of these intensities are reproducible, and a permanent working curve may be constructed. The spectral photometry consists of three steps for analysis: first, the calibration of each spectrogram as referred to above; second, the evaluation of the spectral intensities from photographic blackenings; and third, the deduction of the concentrations from the working curve.

The method outlined in this paper deals particularly with photographic spectral photometry. Fig. 4 shows the characteristics of a spectrogram through a series of H and D curves. The spectrum for each concentration in a series of standard samples was photographed on this plate. This spectrogram was made by a standardized spectrographic and photographic technique and the results used for the construction of a working chart.

EXPERIMENTAL

Apparatus and Materials.

A quartz spectrograph of medium dispersion was found suitable for this work. A dispersion of 2100-7000 Å required a ten inch plate. Instruments with more dispersion are necessary when the spectral frequencies involved are not clearly separated from the frequencies of other elements present. A medium quartz Bausch and Lomb spectrograph was found satisfactory for the application involved.

The electrode holders and arc stand must have a means of conveniently raising and lowering each electrode vertically and have a lateral adjustment for alignment with the optical path.

The rotating adjustable sector was driven by a motor and mounted on the optical bench, placed between the slit and the source.

The electrical circuit consisted of a voltmeter and ammeter with a variable resistance to adjust the current furnished by a 300 volt 15 ampere D-C motor generator set.

The photographic blackenings were determined with a Bausch and Lomb comparator. Some modifications of this instrument were found helpful in obtaining reproducible values for line blackenings. These modifications will be discussed later in the paper.

Eastman processing materials and spectrographic plates were used.

Arc Electrodes.

Spectrographic graphite rods, 5/16 inch in diameter were used for electrodes. The regular Acheson graphite rods were usually employed. These rods contain certain impurities which sometimes cause error but were found sufficiently pure for many applications. Higher quality rods may be purchased for special uses. In routine practice the regular rods may be given a purification treatment. Satisfactory methods of purification have been described by Standen and Kovach (**Standen, G. W., and L. Kovach, Proc. A. S. T. M. 35, II (1935)**). Such methods have been found very useful in the preparation of electrodes for other work in this laboratory. One end of these rods of convenient length for arcing must be recessed sufficiently to receive the sample. Rods treated for purification are more porous than untreated rods and do not require as large a recess. This recess or bore may be made with a hand cutting tool, as these rods are pressed graphite. Since this operation, the preparation of electrodes, is too time consuming for routine practice, it was necessary to design a machine tool. The characteristics of, and the variations in, the rods presented a problem which was solved by means of a motor driven recessing tool.

The drawing in Figure 1 shows the assembly of the tool, which was made of machine steel. The cutting tool, a drill designed to machine a cavity of the size and shape desired, is set in a special chuck. This chuck has a cutting face for machining the end of the graphite rod. The outside diameter of the chuck is standard for the inside bore of the body. It is interchangeable with other chuck assemblies which may be needed for various types and sizes of cavities and for larger or smaller diameter rods. This chuck assembly is held in the proper position by means of a set screw in the body of the tool. The third part of the assembly is an adapter bushing which acts as a bearing and as a means of centering the graphite rod. The outside taper of this adapter bushing is standard, as several such bushings are necessary for various diameter graphite rods used in spectrographic analysis. The parts when assembled make a simple tool which will stand long usage without showing a loss in efficiency, since the graphite rod cuts easily and is a self-lubricant for the steel bearing.

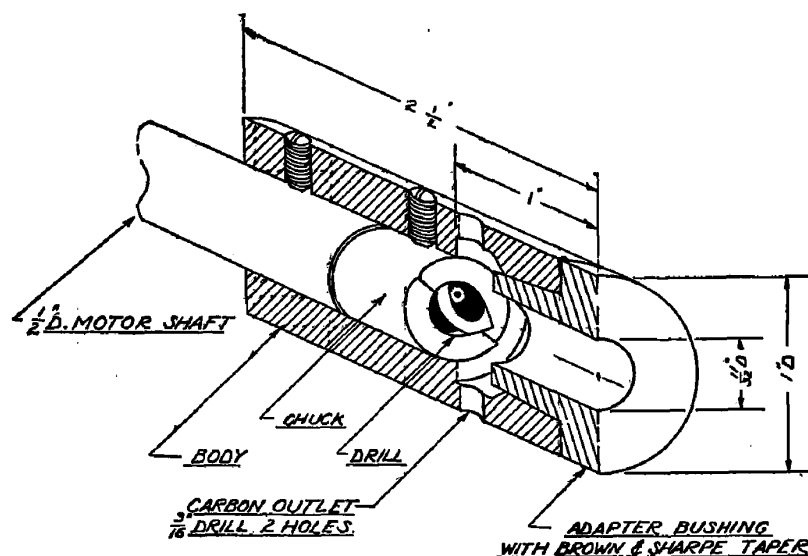


Figure 1 GRAPHITE ELECTRODE RECESSER

This tool can be mounted on the shaft of a small motor and fixed in place with a set screw as shown in the drawing. The rods may be machined by inserting them into the tool: an operation similar to that of sharpening a lead pencil. This tool carefully made of suitable materials will serve its purpose without contaminating the graphite rod with iron sufficiently to appear in the spectrum of the sample. If the electrodes require a purification treatment the drilling is carried out previously.

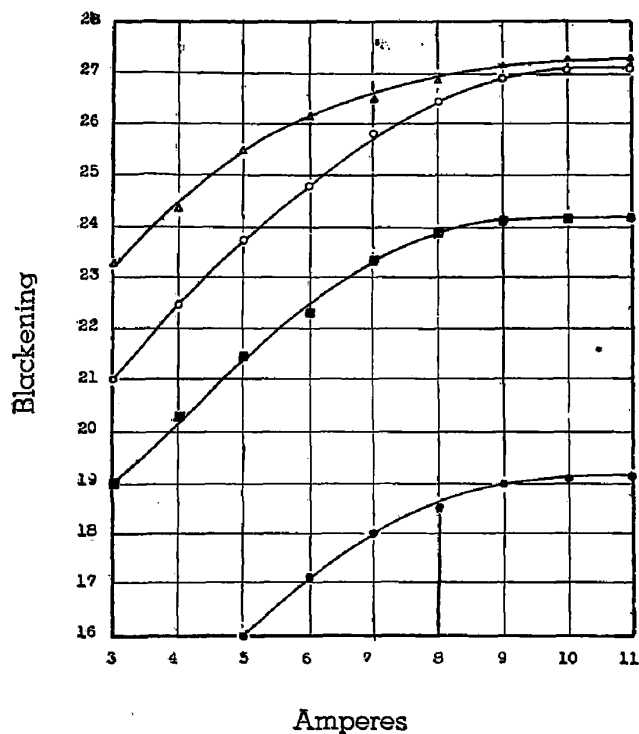


Figure 2—Curves showing spectral blackening vs. excitation current for the following frequencies.

- Δ—Beryllium $\lambda 2348.62 \text{ \AA}$
- Copper $\lambda 2369.91 \text{ \AA}$
- Copper $\lambda 2303.13 \text{ \AA}$
- Copper $\lambda 2400.10 \text{ \AA}$

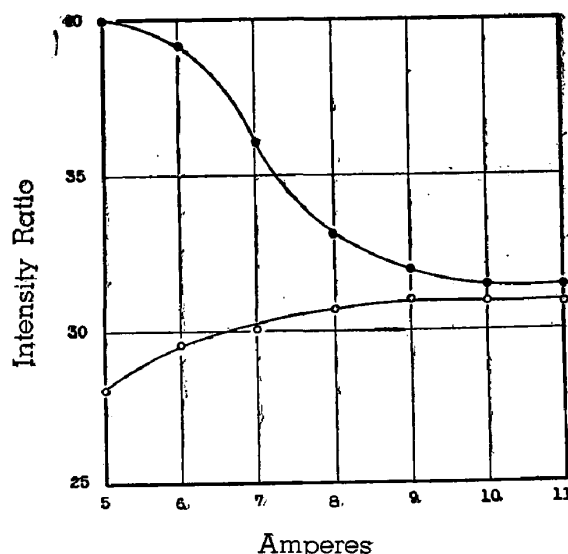


Figure 3—Curves for spectral intensity ratios vs. excitation current.

●— $I_{\text{Be } \lambda 2348.62 \text{ Å}}$ / $I_{\text{Cu } \lambda 2400.10 \text{ Å}}$
 ○— $I_{\text{Cu } \lambda 2369.91 \text{ Å}}$ / $I_{\text{Cu } \lambda 2400.10 \text{ Å}}$

Method of Excitation.

The procedure used in the preparation of standard solutions and samples was essentially that described by Nitchie and Standen (*Nitchie and Standen, Ind. Eng. Chem., Anal. Ed.*, **4**, 182 (1932)). Aliquot portions of 0.1 ml. of hydrochloric acid solution containing 250 grams per liter of the alloy were pipetted into the recess of the graphite electrodes. These electrodes were allowed to dry in an oven at 100° C. for thirty minutes. An arc between two graphite electrodes, the lower being the positive and containing the sample, was excited for sixty seconds at ten amperes with a potential drop of forty volts across an electrode gap of approximately 3/16 inch. At the end of the exposure the sample showed practically complete volatilization from the electrode.

In Figure 2 it may be observed that the blackening of the lines of certain spectral frequencies chosen show an increase in density with an increase in the arcing current. A maximum is approached at ten amperes which is below the maximum density that the plate is capable of recording. At this amperage the emission became almost independent of the small variations in the current or the temperatures of the electrode.

In Figure 3 it may be observed that the ratios of the intensities of certain spectral frequencies of copper and beryllium are practically independent of the current variations at about ten amperes. These variations in the current are limited to about two percent from the mean value. These conditions and results of excitation are reproducible and represent the basis of the modified method of "internal control" (*Gerlach, W., Z. Anorg. Allgem. Chem.* **142**, 389 (1925); *Lundegardh, Die Quantitative Spektralanalyse der Elemente*, Gustave Fisher, Jena (1929); *Gerlach and Schweitzer, Chemische Emissions Spektralanalyse, Grundlagen und Methoden*, Leopold Voss, Leipzig (1930); *Twyman and Hitchen, Proc. Roy. Soc. (London)* **31**, 169 (1930); *Nitchie and Standen, Ind. Eng. Chem., Anal. Ed.*, **4**, 182 (1932)) used in this work. It was found that these conditions were satisfactory for the excitation of the minor constituents being determined. The use of internal control frequencies requires that their intensities bear reproducible ratios with the intensities of the frequency used for the element being determined. This investigation of excitation conditions was carried out in order to determine the arcing conditions which yielded the most reproducible results for the working chart.

Working Chart.

The working chart used in this method of spectrographic analysis is a graphical means of evaluating the concentrations of the elements under test from the photographic blackening of their spectral lines. This chart consists of a series of curves with blackenings as ordinates and relative intensities as abscissae. Figure 4 is the working chart employed in this method for the determination of zinc in copper. The procedure required for the construction of this chart consisted of three steps.

The second step requires that a number of spectra of each concentration of the standard samples be photographed at various sector openings on the plate being calibrated. This plate may be considered the standard spectrogram for the working chart being constructed. If the spectra of more standard samples are required than can be photographed on this standard spectrogram, these exposures may be made on a similar plate and developed in a like manner. The H and D calibration of these subsequent plates is not necessary. The blackening of the frequencies selected for control purposes and of the element being determined were evaluated on the comparator. This data is necessary for the construction of the working chart.

Let this curve be designated the specific curve for one of the control frequencies, such as Cu 3329.62 Å in Figure 4. The proper position of a similar curve for a second control frequency was located in the following manner: blackening values for a second control frequency from the standard samples were plotted against Log E values of the first control frequency of these spectra. In a similar manner the curves may be located for other control frequencies.

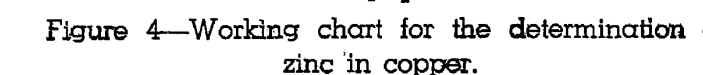


Figure 4—Working chart for the determination of zinc in copper.

This chart also incorporates a satisfactory means of internal control which at the same time compensates for such variations as speed and contrast in photographic plates. When a blackening value of the frequency of an element under test is properly located on the chart, the concentration may be read from a concentration curve or by the correct interpolation between two adjoining curves.

In the construction of the working charts various procedures were investigated for the calibration of the standard spectrogram. A source of continuous light was used for the calibration spectra. The curves were in agreement with those obtained from the copper arc. The Hansen step-diaphragm would have been a convenient means of varying the light from a single exposure for calibration purposes.

In analytical procedures for the determination of more than one unknown, standard solutions may be prepared containing the proper concentrations of each element. In this manner one standard spectrogram may be used to determine the control curves for all the elements present. The required number of working charts may be constructed from this standard spectrogram or from subsequent plates.

Analysis of Samples.

A sample of the copper alloy was dissolved in hydrochloric acid. The volume was adjusted to give a concentration of 250 grams of the alloy per liter. Recessed carbon electrodes were impregnated with the alloy from 0.1 ml. portions of this solution. This process may be accomplished in routine practice with a buret of the type described by Standen and Fuller (**Standen, G. W., and M. L. Fuller, Ind. Eng. Chem., Anal. Ed., 6, 299 (1934)**). The electrodes as described under Apparatus and Materials, were arced at 10 amperes with a potential drop of 40 volts. A rotating sector between the slit and the arc was adjusted to permit the required intensity of the light to enter the slit. The plate was exposed to the emission from the arc containing the sample for the first sixty seconds of the excitation. The plate was developed with a standardized processing technique. The temperature, time, agitation, and developer were essentially the same as used for the development of the plate required for the working chart. The blackening values of two suitable control frequencies and the frequencies of the elements being estimated were evaluated on the comparator. The control frequency blackenings located on the curves of the working chart determine a straight line. This line and the blackening value of the frequency chosen for the element under test locate a point on or between two concentration curves. This point represents a concentration of the element under test. The evaluation of this concentration is made as follows:

$$C_x = \log C_x$$

where C_x = concentration sought.

$$\log C_x = (\log C_1 - \log C_2) \left(\frac{d_2 - d_x}{d_2 - d_1} \right) + \log C_2$$

C_1 and C_2 are the concentrations of the curves between which the point is located.

$d_2 - d_x$ = horizontal axial distance between the point and lower curve.

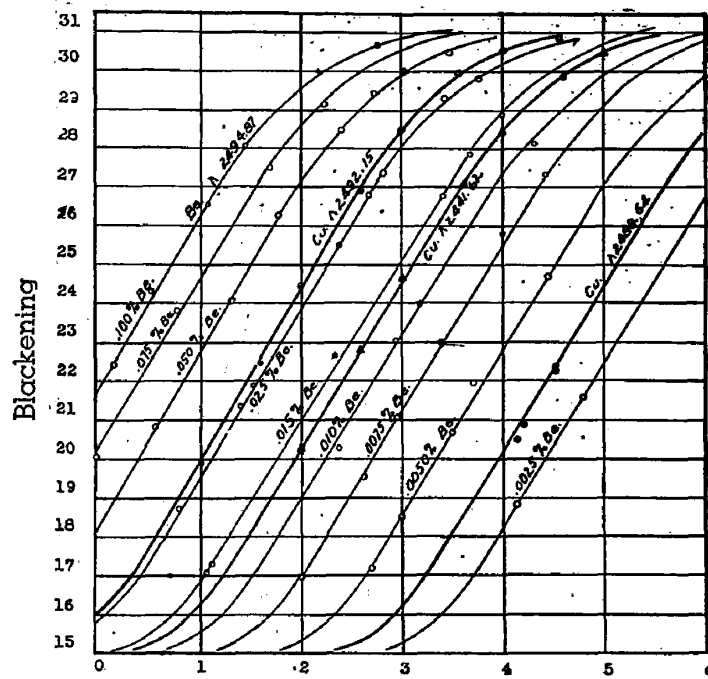
$d_2 - d_1$ = horizontal axial distance between the higher and lower concentration curves.

The calculation of the C_x , the unknown concentration, was simplified by the tabulation of the logarithms of the concentrations of the standard samples and the differences between the logarithms of successive concentrations.

Copper alloys containing aluminum, tellurium, beryllium, cadmium and zinc were analyzed by the above procedure. These metals were present as minor constituents in copper. No difficulty due to the interference of the spectral frequencies was encountered. The standard samples were prepared containing various amounts of each of these metals and copper. A series of copper solutions containing these five elements at different concentrations was tested spectrographically and found to be satisfactory for use in the preparation of the working charts. In Table I are shown the frequencies used for the concentration and control curves of the elements under test for the charts in Figures 4, 5, 6, 7, and 8. The wavelengths of the frequencies are given in International Angstrom Units.

TABLE I

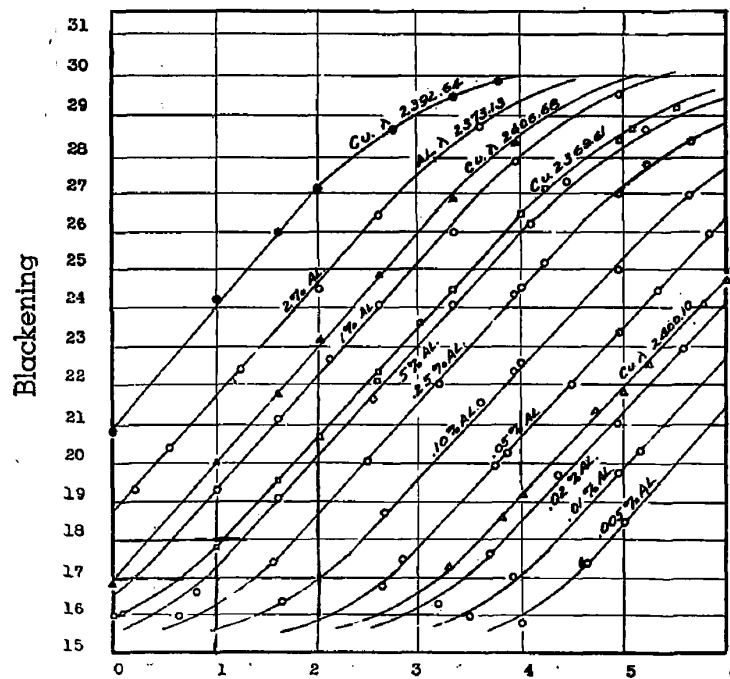
Test Element	Al	Te	Be	Cd	Zn
Frequency of					
Test Element	2373.12	2385.78	2494.87	2288.03	3345.05
Frequencies of					
Copper control	2369.91	2354.63	2492.15	2303.13	3349.26
for the test	2392.64	2369.91	2441.62	2276.26	3329.62
element	2406.68	2400.10	2489.64		3354.47



Log. ₂ E

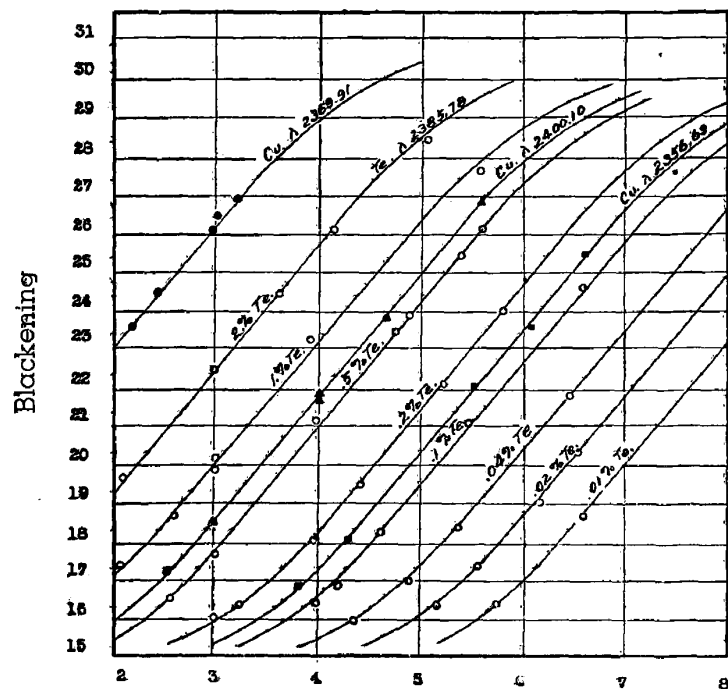
Figure 5—Working chart for the determination of beryllium in copper.

These values used to identify the frequencies were published by H. Kayser (**Kayser, H., Tabelle der Hauptlinien der Linienspektren aller Elemente, Julius Springer, Berlin (1926)**). The photographic blackening values of these frequencies were evaluated for each sample. Two exposures were made for each sample, one being of a higher intensity than the other. This practice gave at least one spectrum with blackening values for each element that were in the straight line section of the H and D curve. The analyses carried out were within the range of concentrations shown in Table II.



Log. ₂ E

Figure 6—Working chart for the determination of aluminum in copper.



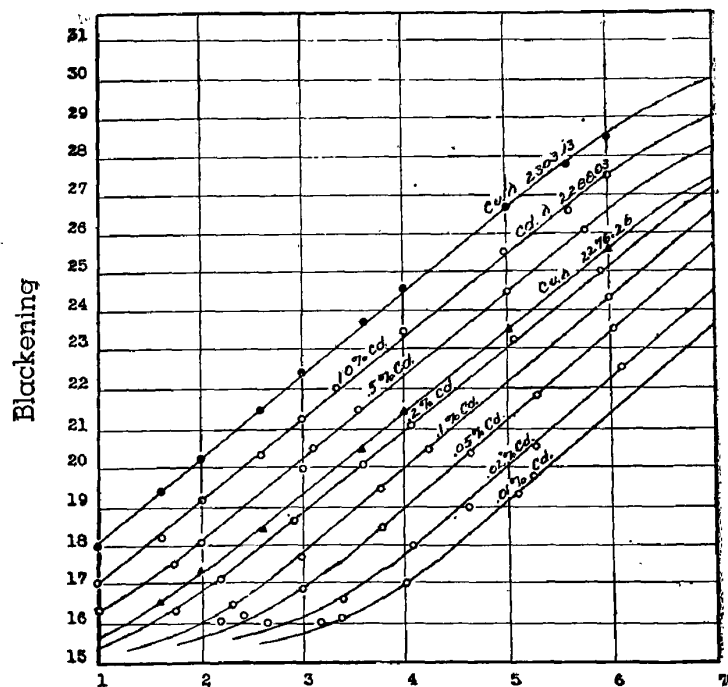
Log. ₂ E

Figure 7—Working chart for the determination of tellurium in copper.

TABLE II

	Al	Te	Be	Cd	Zn
Minimum Conc.	0.005%	0.01%	0.0025%	0.01%	0.02%
Maximum Conc.	2.0 %	2.0 %	0.10 %	1.0 %	4.0 %

The quantitative determination of these metals in copper is not limited to the concentrations shown in Table II.



Log. ₂ E

Figure 8—Working chart for the determination of cadmium in copper.

A measure of the accuracy of the analysis of one hundred successive determinations may be observed from the results shown in Table III. The mean error encountered for all trials was less than 5.0%, including the unfavorable results in brackets. The untreated graphite rods of the quality used in this work, together with some uncertainty of the excitation conditions, make such results unavoidable. The errors in this work are attributed in the greater part to variables in the excitation and may be minimized through the use of electrodes of the alloys. Preliminary experiments with copper alloy electrodes as standards and specimens indicate that the excitation conditions may be controlled with a higher degree of accuracy and more dependability than for graphite rods and solutions. However, the graphite electrodes permit lower limits of detection of certain elements in copper than have been obtained from metallic electrodes due to the higher temperatures attained for a given amperage. Thus the advantages, previously pointed out, resulting from the use of graphite rods, were of sufficient importance to warrant their use in this work.

TABLE III

Spectrographic determination of minor constituents of copper.

Copper Alloy Sample Number	Element Determined	Amount Added Percent	Amount Found Percent
1a	Be	0.0050	0.0053
1b	Be	0.0050	0.0052
1c	Be	0.0050	0.0052
2a	Be	0.0075	0.0074
2b	Be	0.0075	0.0073
2c	Be	0.0075	0.0073
3a	Be	0.0100	0.0107
3b	Be	0.0100	0.0100
4a	Be	0.0150	0.0151
4b	Be	0.0150	0.0153
4c	Be	0.0150	0.0150
5a	Be	0.0250	0.0255
5b	Be	0.0250	0.0247
6a	Be	0.0500	0.0500
6b	Be	0.0500	0.0485
7a	Be	0.0112	0.0113
7b	Be	0.0112	0.0102
7c	Be	0.0112	0.0106
8a	Be	0.0165	0.0154
8b	Be	0.0165	0.0160
9a	Be	0.0075	0.0073
9b	Be	0.0075	0.0071
9c	Be	0.0075	0.0076
10a	Be	0.0200	0.0193
10b	Be	0.0200	(0.0170)
10c	Be	0.0200	(0.0172)
11a	Be	0.0100	0.0093
11b	Be	0.0100	0.0100
11c	Be	0.0100	0.0094
12a	Be	0.0375	0.0379
13a	Be	0.0087	(0.0097)
13b	Be	0.0088	0.0092
13c	Be	0.0088	0.0082
14a	Be	0.0063	0.0065
14b	Be	0.0063	0.0065
15a	Be	0.0125	0.0124
15b	Be	0.0125	0.0124
16a	Be	0.0263	0.0272
16b	Be	0.0263	0.0257
17a	Be	0.0225	0.0233
17b	Be	0.0225	0.0223
17c	Be	0.0225	0.0227
18a	Be	0.0288	0.0299
18b	Be	0.0288	0.0280
18c	Be	0.0288	0.0298
19a	Be	0.0137	0.0145
19b	Be	0.0137	0.0132
20a	Be	0.0162	0.0147

TABLE III (Continued)

20b	Be	0.0162	(0.0144)
21a	Be	0.0287	0.0286
22a	Be	0.0275	0.0260
22b	Be	0.0275	0.0299
22c	Be	0.0275	0.0264
23a	Be	0.0080	(0.0088)
23b	Be	0.0080	0.0078
23c	Be	0.0080	0.0085
24a	Be	0.0043	0.0042
24b	Be	0.0043	0.0043
24c	Be	0.0043	0.0043
25a	Be	0.0075	0.0073
25b	Be	0.0075	0.0076
26a	Al	0.625	0.640
26a	Ca	0.500	0.546
26a	Zn	1.250	1.150
26b	Al	0.625	0.670
26b	Te	1.250	1.300
26b	Zn	1.250	1.190
27a	Al	0.550	0.510
27a	Ca	0.350	0.320
27a	Zn	1.100	1.050
28a	Al	0.175	0.160
28a	Ca	0.350	0.330
28a	Zn	0.350	0.375
28b	Al	0.175	0.180
28d	Ca	0.350	0.360
28b	Te	0.350	0.343
28b	Zn	0.350	0.350
28c	Al	0.175	0.185
28c	Ca	0.350	0.380
28c	Te	0.350	0.376
28c	Zn	0.350	0.380
29a	Al	0.300	0.270
29a	Ca	0.600	0.550
29a	Zn	0.600	0.570
29b	Al	0.300	0.320
29b	Ca	0.600	0.640
29b	Te	0.600	0.630
29b	Zn	0.600	0.630
30a	Al	0.150	0.142
30a	Ca	0.550	0.520
30a	Te	0.550	0.590
30a	Zn	0.550	0.510
31a	Al	0.525	0.560
31a	Zn	1.050	1.000
31b	Al	0.525	0.500
31b	Ca	0.300	0.280
31b	Te	1.050	0.970
31b	Zn	1.050	1.080
31c	Al	0.525	0.550
31c	Te	1.050	1.100

Discussion.

A material may be heated to incandescence by means of an arc, spark, or flame. The arc may be used between electrodes containing the material. In this work electrodes impregnated with a solution of the alloy were used for analysis. This operation was carried out by a solution technique which offered some advantages over the use of metallic electrodes (Nitchie, C. C., *Ind. Eng. Chem., Anal. Ed.*, **1, 1 (1929)**). By this procedure representative "unknown" and standard samples were conveniently and accurately obtained. A 50 gram sample may be dissolved and only 0.1 ml. portions of this solution used, obviously representative of the sample. The preparation of copper alloy electrodes of known concentration is a difficult and tedious procedure for the metallurgist and a representative sample is

difficult to obtain for analysis. An arc between carbon electrodes reaches a very high temperature which heats the vapors of the sample to incandescence as volatilization from the electrode takes place. The sample was volatilized from the electrode in a relatively short arcing period. Through careful selection of the exposure time and the arcing current, the rate of vaporization of each minor constituent to that of the principal material was found to be reproducible from electrodes prepared by a standardized technique. Some conditions of arcing, such as wandering of the arc about the electrodes, caused poor reproducibility of the intensity of the spectrum. It was found that the intensity of the spectral frequency of the element under test varied with the intensities of certain spectral frequencies of the principal element present. This means of internal control was used to compensate for the variable.

In some applications internal control has been effected more satisfactorily through the use of a frequency or frequencies of an element added as an internal standard (**Gerlach and Schweitzer, Foundations and Methods of Chemical Analysis by the Emission Spectrum, Adam Hilger, Ltd., London (1930)**) in a known concentration to the solutions of the samples. Certain frequencies of the principal element of the alloy were found reliable in this investigation. These frequencies are represented on the working charts as H and D curves. These curves have another function in addition to that of internal control of intensity. This second function is a means of control of the speed and contrast of the emulsion of the spectrogram. It was found that the single coated emulsion plates when exposed for calibration purposes and properly developed gave a characteristic H and D curve which in the range of certain spectral frequencies was a straight line function except near the maximum and minimum blackenings. The linear section of this curve represented the characteristics of the emulsion, but the curved sections near the maximum and minimum blackenings were not reliable. This straight line section of the H and D curve was therefore reproducible between certain blackening limits.

Two characteristics of an emulsion, the speed and the contrast, were found to vary somewhat from plate to plate. The standardized processing technique used for development of the emulsion reduced these variations considerably. The working chart was so arranged that the variations in the speed of the emulsion have no effect on the results as long as the density values of the frequencies are on the straight line section of the curves. However, variations in the contrast of the emulsion had to be treated by a method of calibration control incorporated on the chart with internal control. The actual functioning of this method of control involves the use of H and D curves. These curves must have a straight line section. The flexibility of this means of control depends greatly upon the length of this section of the curve. The materials and the photographic developing practices used determine to a great extent the nature of the curve.

Satisfactory H and D control curves are shown in Figure 9 for three plates calibrated with line spectra from a copper arc. The curves for Plate I were considered the control curves for Plates II and III. These curves were constructed in a manner similar to the control curves for the working chart used in this method. Plates I and II were selected from the same box of new plates, exposed and developed under standardized conditions for routine practice. The curves for Plates I and II in Figure 9 show very similar characteristics. Plate III was selected from another type of single coated emulsion. The curves for this plate show that both the speed and contrast of the emulsion are somewhat different than the same characteristics of Plate I. However, blackening values from Plate III can be applied to the control curves of Plate I with a reliability comparable to that of applying these same values to the curves which represent the emulsion of Plate III. In Figure 9 such values from a spectrum of Plate III are applied to the respective curves for Plate I taken as a standard spectrogram. The result is that two of these values determine the straight line A' which passes through the third curve at a blackening value corresponding to the value recorded for the third frequency on Plate III. Hence such a point may be located for concentration curves by using the control blackening values to locate a line such as A' and then applying the blackening value of the frequency for the element under test to this line. This point may be evaluated in terms of the adjoining concentration curves as constructed for the working charts.

The curves, however, in Figure 9 for Plates I and II represent results which were in general reproducible. The blackening values of Plate II applied to the control curves of Plate I determine such a line as A which is perpendicular to the intensity axis and has an intensity value in terms of Plate I. It is therefore possible to locate this line with one control value, using a second value to check the reliability of the practice. If the plates are not of the same contrast the second control blackening value will obviously determine a straight line inclined to the axis. The dependability of using this line may be checked by applying a blackening value of a third control frequency to its curve. This point should also be on the same straight line determined by the first two values. This practice, as demonstrated in Figure 9, should compensate for the variations in contrast and speed when encountered and check the reliability of using the H and D curves as straight lines within the limits of certain blackening values. These limits and variables encountered depend considerably on the photographic materials and technique used.

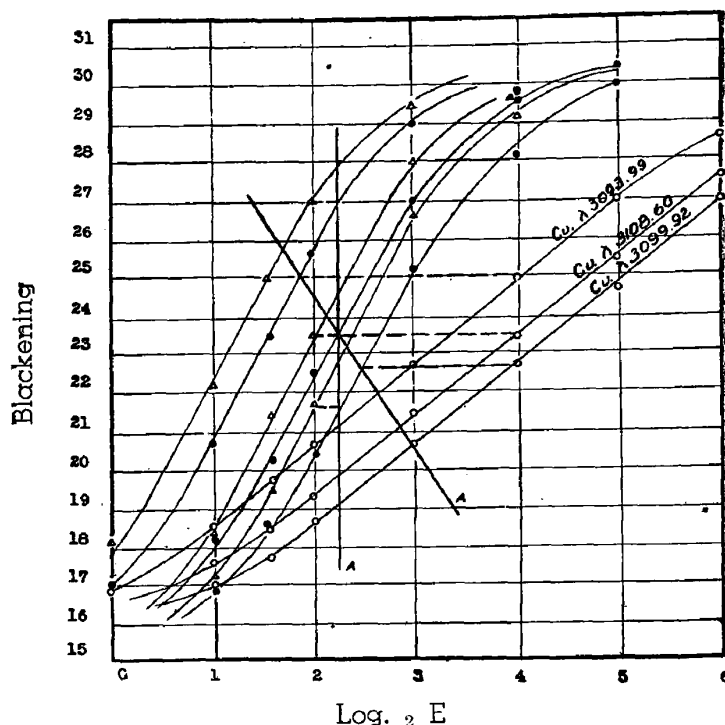


Figure 9—Chart demonstrating a method of exposure and photographic plate control.

- —Copper control curves for Plate I.
- △ —Copper control curves for Plate II.
- —Copper control curves for Plate III.

In order to select the most suitable materials available certain factors must be considered. The most important characteristics of the photographic emulsions are the speed and contrast. In actual practice the intensity of the illumination can be adjusted in accordance with the exposure time utilized and the speed obtained from the photographic materials. The contrast, therefore, is the important factor for consideration.

Consider the hypothetical characteristic curves shown in Figure 10. Neglecting the speeds of these two materials the important difference lies in the contrast, gamma, the slope of the characteristic curve. Assuming such physical characteristics of these two emulsions as graininess, turbidity, absorption, and resolving power to be the same, the higher contrast of emulsion A makes it the more desirable in quantitative analysis for a short range of concentrations where high accuracy is necessary. Emulsion B may be more desirable than A where the samples vary over a long range of concentrations. However, the differential in the blackening for a given change in concentration is necessarily lower for the lower contrast emulsion.

In general the quantitative applications require a plate with a high contrast emulsion. It has been pointed out that the contrast changes in accordance with the frequency or frequencies of the light to which the emulsion was exposed. It follows, then, that the characteristic curve of the emulsion represents the photographic response to light in certain sections of the spectrum. Hence an emulsion should be chosen with the proper contrast in the region of the spectral frequencies used. It is desirable to select a plate which has the same, or if necessary, a slowly changing contrast over that section of the spectrum for which it is suitable. It may be found necessary in some applications to use more than one emulsion, since frequencies in the visible range may be needed for one constituent and another emulsion for an element in the ultraviolet region. Some of the plates used in regular practice may be made sensitive to ultraviolet, visible, and red light by the proper treatment.

The final step in the selection of an emulsion or its treatment is the construction of an H and D calibration curve for the spectral range involved. The plate selected should have the desired contrast and give a long straight line section curve. The blackening values on the straight line section of the characteristic curves were found more reliable than those near the limiting values. For this reason the blackenings recorded were limited by certain maximum and minimum values. The processing technique and developing materials used depended upon the emulsion characteristics. Since many developers are affected by temperature and agitation, these conditions were standardized for the type of plate used. The developer was replenished for each processing care being taken to use precisely the

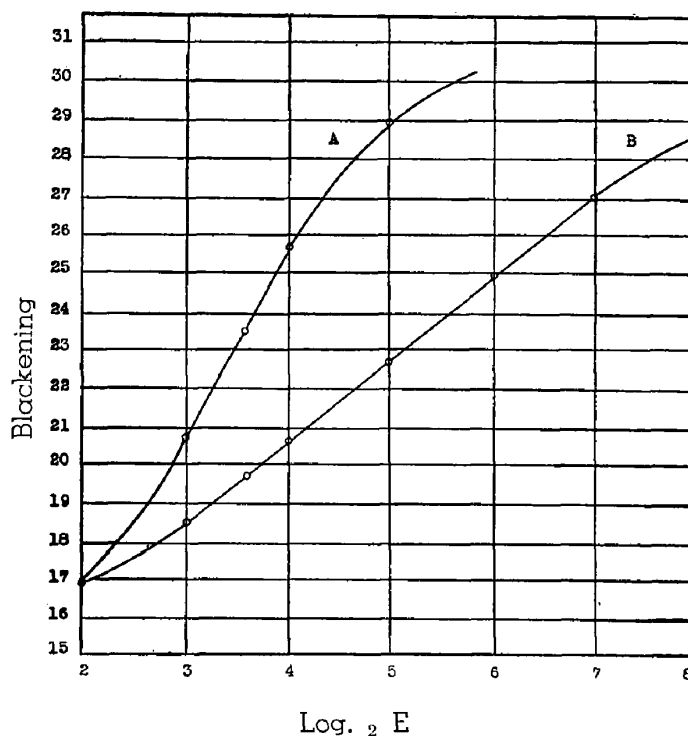


Figure 10—Characteristic H and D curves of two types of photographic emulsions for spectrochemical analysis.

same concentration. The straightness and length of the straight line section of the calibration curve depends greatly upon the proper digestion of the emulsion. This digestion problem varies considerably with the emulsion used and the method of agitation. If a double coated emulsion is used the two layers may not have the same contrast. This feature makes it inadvisable to use any plates except single coated emulsions for work which depends on a straight calibration curve.

The blackening values used in this work were evaluated with a density comparator. The image to be measured was brought to a focus on a screen. The optimum intensity of the illumination through a clear portion of the plate was adjusted to give a predetermined deflection of a galvanometer in a circuit with a photronic cell installed back of a slit in the screen. An iris diaphragm properly placed in the projection system will allow this adjustment. The deflection of the galvanometer caused by the light which passed through the darkest portion of the image was recorded as the blackening value. A variable resistance in parallel with the cell was used to compensate for variations in the cell resistance or sensitivity. Through these modifications and the proper calibration of the density comparator as shown by scale readings, it was found possible to record galvanometer deflection readings as blackening values. These values are reproducible and have proved to be a linear function of the blackness of the image. Errors caused by the variations of the line voltage used for illumination were minimized by the use of a voltage regulator.

Summary.

I. A method of spectrographic analysis of general application has been outlined. It is exemplified by the quantitative determination of beryllium, cadmium, aluminum, tellurium, and zinc; present as minor constituents in copper alloys of these metals.

II. A new procedure of "photographic plate control" incorporating internal control of intensities for spectral frequencies is demonstrated.