



Designation: E 158 – 86 (Reapproved 1996)^{ε1}

Standard Practice for Fundamental Calculations to Convert Intensities into Concentrations in Optical Emission Spectrochemical Analysis¹

This standard is issued under the fixed designation E 158; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Keywords were added editorially in June 1996.

1. Scope

1.1 This practice covers fundamental forms of plots, used to convert measured intensities into concentrations in both photographic and direct reading analysis. It includes equations suitable for use with calculators or computers for such conversions, and methods for making background corrections and corrections for interferences from other elements.

1.2 A previous issue of this practice attempted to treat optical emission and X-ray fluorescence as one field, employing similar calculations to convert measured radiation intensities into concentrations. In fact, quite different procedures are used in the two fields. This practice confines itself to optical emission spectrochemical analysis. A separate practice will be devoted to calculations in X-ray fluorescence spectroscopy.

1.3 This practice is related to but should be distinguished from:

1.3.1 Practice E 116E 116, which describes procedures for converting either transmittance or optical density of lines on a photographic emulsion into intensities or relative intensities. This step is required in photographic analysis before the present practice can be applied.

1.3.2 Practice E 305E 305, which describes the procedures for fitting a curve to a group of plotted points, and for standardizing the equipment, in order to obtain optimum accuracy, guided by sound statistical practice.

1.3.3 Practice E 876E 876 discusses the statistical treatment commonly applied to spectrochemical data, such as calculating the standard deviation and the relative standard deviation.

1.4 This practice includes the following sections:

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1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- E 116 Practice for Photographic Photometry in Spectrochemical Analysis²
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²
- E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves²
- E 876 Practice for the Use of Statistics in the Evaluation of Spectrometric Data³

3. Terminology

3.1 For definitions of terms used in this practice, refer to Terminology E 135E 135.

4. Significance and Use

4.1 Over the years, many workers have developed improved methods for plotting the measured intensities obtained from chemically analyzed specimens (“standards”), and for calculating concentrations of unknowns from the “analytical” curves obtained. This practice describes the methods of plotting and the calculation techniques which have been found to produce superior results.

¹ This practice is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.22 on Statistics and Quality Control.

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² Annual Book of ASTM Standards, Vol 03.05.

³ Annual Book of ASTM Standards, Vol 03.06.

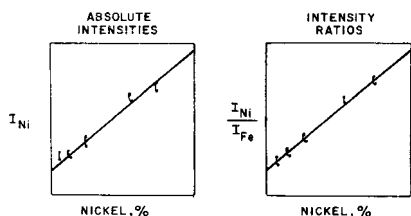


FIG. 1 The Advantage of Using an Internal Standard

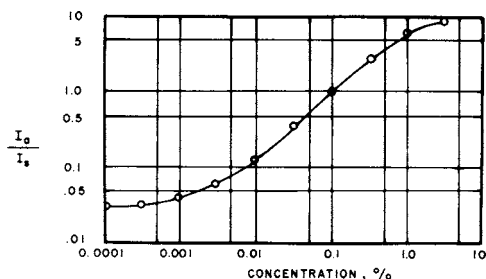


FIG. 2 Log-Log Plot

5. Fundamental Theory

5.1 In optical emission spectrochemical analysis, there are relatively few interferences from other elements, for materials with spectra of normal complexity, provided that a spectrograph or spectrometer with adequate dispersion and resolution is used, and that analytical lines are selected carefully. In general, the intensity of an analytical line is a function only of the concentration of the element that produces it. Therefore, it is common practice to employ an individual analytical curve for each element in a matrix. Observed intensities are converted into concentrations directly from this curve, without any correction for other elements. However, at times, it may be desirable to apply corrections for background or for interferences from other elements, as discussed later in this practice.

5.2 *Internal Standard Method*—In the early days of quantitative optical emission spectrochemical analysis, Gerlach and Schweitzer⁴ found that when they measured the “blackness” of lines produced on photographic emulsion by a series of chemically analyzed materials and plotted them against their known concentrations, quite erratic results were obtained. A single specimen gave different “blacknesses” when run repeatedly. These variations were ascribed to erratic excitation and to variations in illumination. If they measured a line of an “internal standard element” that had the same concentration in all their materials, they could measure these exposure variations. Ratios determined by dividing the “blackness” of an analytical line by the “blackness” of an internal standard line, gave more repeatable results when the same material was burned repeatedly. Plots of “blackness” ratios versus concentration produced analytical curves with a better fit of points. Fig. 1 illustrates the advantages in precision and fit of points to a curve obtained by the internal standard technique, when applied to the determination of nickel in low-alloy steels. Curves plotted on linear graph paper are used for illustration.

⁴ Gerlach, W., and Schweitzer, E., *Foundations and Methods of Chemical Analysis by the Emission Spectrum*, Adam Hilger, Ltd., London, 1929.

5.2.1 Over the years, power supplies for sampling and exciting materials have become much more stable, and exposure variations have been reduced, but in general, the internal standard procedure still produces better results than the use of absolute intensities. Accordingly, the method is employed almost universally.

6. Plotting Analytical Curves with a Constant Internal Standard

6.1 *Log-Log, Linear, and Log-Linear Plots*—Different plotting methods produce analytical curves of widely different appearance. Each has its own advantages. Fig. 2, Fig. 3, and Fig. 4 illustrate the curves most commonly employed. The characteristics of each are listed. It should be emphasized that a knowledge of the theoretical shape of a curve can assist in deciding how best to fit a curve to an array of plotted points.

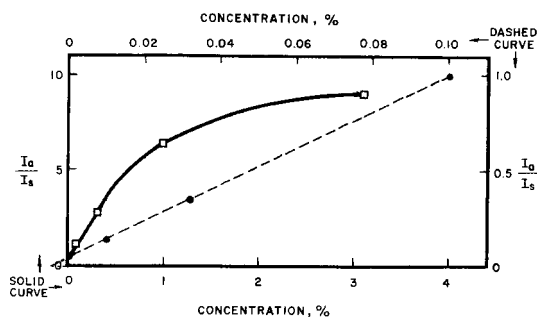


FIG. 3 Linear Plot

6.2 *Theoretical Data*—The theoretical data used to plot the curves are presented in Table 1. It is assumed that throughout the series of measurements the ratio of the intensity of the background to the intensity of the internal standard line remains constant, at 0.030. At low concentrations, the ratio of the intensity of the analytical line to the intensity of the internal standard line (I_a/I_s) is assumed to vary in direct proportion to the concentration. At 0.01 %, (Column 2), it is assumed to measure 0.100 (Column 3); therefore at 0.0032 %, it will measure 0.032, etc. The total signal is the sum of the intensity ratios of the background and line. Thus, at 0.01 %, it is 0.130; at 0.0032 %, it is 0.062, etc. The table first lists concentrations down to 0.0001 %, where the line signal is 0.001, and the background, 0.030. Then the table lists increasing concentrations. At 0.32 %, it is assumed that self-absorption is significant, so that the line response is not as great as the increase in concentration. The data tabulated in Column 5 are explained later in 6.5.1.

6.3 *Characteristics of Log-Log Plots*—Fig. 2 shows the appearance and major features of a log-log plot. The intensity ratios of the total signal (Column 4, Table 1) are plotted against concentrations (Column 2), using log-log graph paper. In the illustration, intensity ratios are plotted vertically, since these are measured, and concentrations horizontally, since they are known (at the time of plotting the curve). However, some workers prefer to reverse the scales.

6.3.1 Below the detection limit, the curve starts as a horizontal line, corresponding to the spectral background. The curve rises slowly as the line signal can be distinguished from the background.

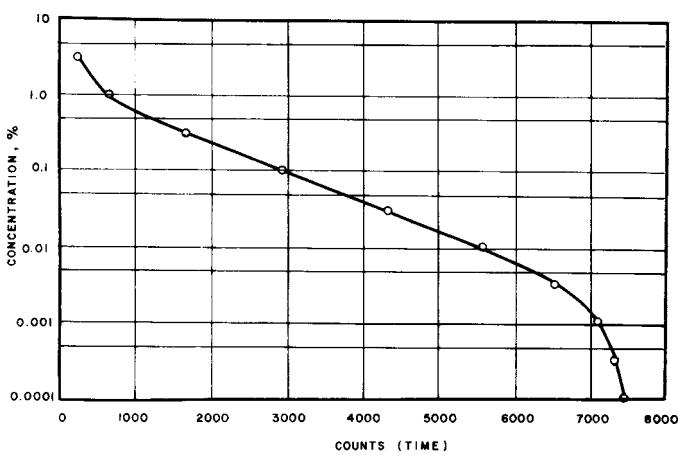


FIG. 4 Log-Linear Plot

TABLE 1 Theoretical Data for Log-Log, Linear, and Log-Linear Plots

1	2	3	4	5
Std. No.	%	Intensity Ratio, Line Alone	Intensity Ratio, Line + Background (Col. 3 + 0.030)	Time (t) + 3000 (See 6.5.1)
1	0.01	0.100	0.130	5601
2	0.0032	0.032	0.062	6545
3	0.0010	0.010	0.040	7104
4	0.00032	0.0032	0.0332	7342
5	0.00010	0.0010	0.031	7429
6	0.032	0.316	0.346	4353
7	0.10	1.000	1.030	2962
8	0.32	2.800	2.830	1674
9	1.00	6.300	6.330	647
10	3.12	8.900	8.930	208
Supplementary Points (See Fig. 6)				
11	0.008	0.080	0.110	
12	0.0065	0.065	0.095	
13	0.005	0.050	0.080	
14	0.0024	0.024	0.054	
15	0.0015	0.015	0.045	

the background. At approximately 0.01 %, the curve becomes a straight line at, or close to, a slope of 45°. In other words, when the background becomes a small part of the signal, doubling the concentration approximately doubles the intensity ratio. In a spark or d-c arc, the curve develops a “shoulder” as a result of self-absorption, at 800 to 3000 times the detection limit, depending on the individual spectral line. Hollow cathodes, glow discharges, inductively coupled plasmas, or similar sources may continue a straight line response over a much greater range.

6.3.2 For a spark or an arc, because of the “toe” and “shoulder,” three-cycle log graph paper is usually adequate to record the intensity range even though four or five cycles may be needed to record the concentration range.

6.3.3 The scales of log-log graph paper are preselected. Photographically, if the intensity ratios have been determined properly, as specified in Practice E 116E 116, the shape and slope of a log-log plot of intensity ratios versus concentration are not affected by the contrast of the photographic emulsion or the conditions of development. When using a direct-reading

spectrometer, the voltage applied to the dynodes of the photomultiplier, or the gain of an amplifier, will determine the background level, but will not affect the shape or slope of a log-log plot. Accordingly, a log-log plot can show whether a spectrograph or a direct reading instrument is performing as theory would predict.

6.3.4 Analytically, a log-log plot provides an open scale at low concentrations, and equal readability at 0.0001 % or 1.0 %. This is valuable when the concentration range exceeds two orders of magnitude. Log-log plots are most useful when the ability to read low concentrations is relatively more important than accurate readings at high concentrations. An example would be the analysis of geological samples with a d-c arc, where an element may vary from 0.001 % or less, to 1.0 % or more, but the relative precision will never be better than 5 % of the amount present. Note, however, that a log-log plot is compressed at high concentrations, such as in measuring carbon in cast iron in the 2 to 4 % range, where the readability should be 0.01 % or better.

6.3.5 Instrumental variables, such as dirty optics, may introduce a proportional reduction in the intensity. For example, there may be a 10 % loss at all intensity levels. Cleaning the condensing lens or window may restore the original response. Such changes are compensated for by “standardizing” the instrument. On a log-log plot, such changes produce an upward or downward parallel shift of the curve. In a direct-reading spectrometer, the original response can be restored by a “gain” adjustment.

6.3.6 A change in the background level will result in a rotation of the curve and a change in its shape. There will be almost no effect at high concentrations, but a very significant change at low concentrations.

6.4 Characteristics of a Linear Plot—Fig. 3 shows the major features of a linear plot. The intensity ratios are plotted against concentrations using linear graph paper. The solid line shows the complete plot, using the left-hand and bottom scales. The low-concentration portion of the curve (dashed line) is plotted on an enlarged scale using the top and right-hand scales.

6.4.1 The linear graph gives a very open plot at high concentrations. However, it cannot be read with desired precision at low concentrations (below about 5 % of full scale). Larger graph paper helps, but even with 50-cm paper it is not possible to read to two-figure precision below 1 % of full scale. Wider concentration ranges should be plotted in segments, with expanded scales for the lower concentrations, as shown in the illustration.

6.4.2 At low concentrations, the plot is a straight line, starting at the background reading for zero concentration. At high concentrations, the self-absorption becomes apparent more quickly than in a log-log plot, and the curve flattens more dramatically. The straight-line response makes a linear plot particularly appropriate to fitting a curve through points that tend to scatter at low concentrations, where the precision becomes poor. Also, if there are points for intermediate concentrations that fall significantly above the straight line established by the lowest and one of the higher concentrations, this is a clear indication of probable interference from other

element. The distance above the line is a measure of the amount of interference.

6.4.3 Instrumental changes such as dirty or cleaned optics, which result in proportional loss or gain in intensity, produce a rotation of the curve. The rotation is about the intercept with the zero intensity ratio axis, which is shown by the dashed line of Fig. 3. On a direct-reading spectrometer, a “gain” change can compensate, and restore the curve to its original slope.

6.4.4 On linear plots, background changes produce vertical curve shifts.

6.5 *Characteristics of Log-Linear Plots*—Log-linear plots are employed with the type of readout system that has a logarithmic response. The commercial version utilizes the time that is required by the internal standard capacitor, or its equivalent, to fall to the voltage accumulated on an analytical capacitor. The logarithmic time decay is represented by the equation:

$$E_i = E_0 e^{-t/k} \quad (1)$$

where:

E_i = the voltage accumulated on the analytical capacitor,

E_0 = the voltage on the internal standard capacitor,

t = the time required for E_0 to decay to E_i , and

k = the RC constant determined by the product of the capacitance and the bleeder resistance of the circuit.

Long times, or high digital counts, represent low concentrations; short times, or low counts, correspond to high concentrations. Thus, the circuitry produces a negative slope. The theoretical slope is the negative reciprocal of the RC constant.

6.5.1 If Eq 1 is converted to natural logarithms and solved for t , then,

$$t = -k \times \ln \left(\frac{E_i}{E_0} \right) \quad (2)$$

In the later commercial instruments with digital readouts, the RC constant, k , is adjusted to 1275 counts. In the fifth column of Table 1, (E_i/E_0) represents the ratio of the intensity of the signal plus background to the intensity of the internal standard. To maintain the readings positive, a bias of 3000 counts has been added. Therefore, Column 5 represents the time, expressed as digital counts:

$$t = 1275 [-\ln (\text{Column 4})] + 3000 \quad (3)$$

For example, the first entry is:

$$1275[-\ln 0.130] + 3000, \text{ or } 1275[-(-2.04)] + 3000 = 5601$$

6.5.2 It is customary to plot concentrations vertically on a logarithmic scale and time or digital counts horizontally. Fig. 4 shows a log-linear plot, using the data from Table 1.

6.5.3 The log-linear plot, like the log-log, has a theoretical response that is independent of instrumental variables so long as the RC constant is maintained the same. Therefore, it shows whether an analytical line is performing as expected. It has a “toe” at the background, changing to a straight line at higher concentrations. A “shoulder” develops if the line starts to show self-absorption.

6.5.4 The log-linear response provides an open scale at low concentrations, and equal readability at all levels. The time scale is compressed at high concentrations.

6.5.5 Instrumental changes that result in a proportional change in intensity produce a lateral shift of the analytical curve.

6.5.6 A change in background alters the shape of the curve at the low-concentration end of a log-linear plot.

7. Plotting Analytical Curves with a Variable Internal Standard

7.1 *Internal Standard Dilution*—In high alloys, where two or more elements vary independently over rather wide concentration ranges, the internal standard will no longer have a constant concentration. For example, in stainless steels, where nickel and chromium vary widely, the iron may have a concentration range from 65 to 75 %. The iron intensity will vary with the iron concentration as well as with the changes in illumination, which it is supposed to measure. Because of this “internal standard dilution,” a specimen with 65 % iron will produce a low-intensity reading for iron, which will give a high-intensity ratio, I_{Ni}/I_{Fe} . The point will fall above the curve. Specimens with unusually high iron concentrations will produce points that fall below the curve.

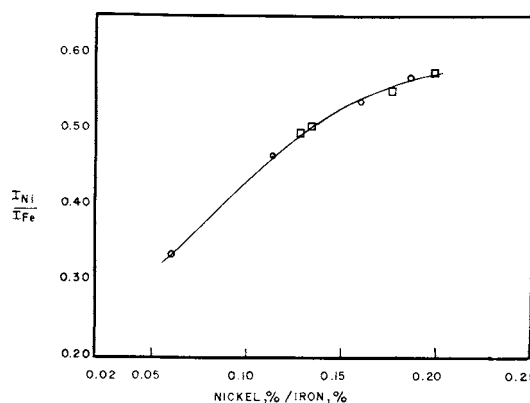


FIG. 5 A Typical Concentration Ratio Plot

7.2 *Concentration Ratio Plots*—To compensate for internal standard variations, intensity ratios are plotted against concentration ratios.⁵ To continue the illustration of stainless steels, if we plot I_{Ni}/I_{Fe} against %Ni/%Fe, the points fall on a smooth curve, as shown by Fig. 5. Linear graph paper is used to obtain an open scale at high concentrations.

7.2.1 Concentration ratio plotting does place the points on a smooth analytical curve, but there is no longer a direct relationship between intensity ratios and concentrations for the elements being measured. The concentration of the internal standard must be determined first, before the concentration ratios can be converted into concentrations. The concentration of the internal standard can be determined by a formula that is based on the fundamental rule that the concentrations measured for all significant elements must add up to 100 %. This is illustrated below for stainless steels, where the element symbols represent their concentrations:

⁵ Coulliette, J. H., “Spectrographic Determination of Nickel and Chromium in Stainless Steel,” *Industrial and Engineering Chemistry*, Vol. 35, 1943, p. 712.

$$\begin{aligned} &C + Mn + S + P + Si + Cr + Ni \\ &+ Mo + Nb + T + Fe = 100 \% \end{aligned} \quad (4)$$

where:

T = the total trace elements not measured.

For example, it might be assumed that copper, cobalt, vanadium, and all other elements not measured would have a nominal value of $T = 0.15 \% \pm 0.05 \%$. Dividing Eq 4 by the concentration of iron (Fe), gives:

$$\begin{aligned} &\frac{C}{Fe} + \frac{Mn}{Fe} + \frac{S}{Fe} + \frac{P}{Fe} + \frac{Si}{Fe} + \frac{Cr}{Fe} + \frac{Ni}{Fe} \\ &+ \frac{Mo}{Fe} + \frac{Nb}{Fe} + \frac{T}{Fe} + \frac{Fe}{Fe} = \frac{100}{Fe} \end{aligned} \quad (5)$$

This can be represented in generalized terms by:

$$\sum \frac{C_i}{C_s} + 1 = \frac{100 - T}{C_s} \quad (6)$$

where:

- C_i = the concentration of the individual analytical elements,
- C_s = the concentration of the internal standard,
- $\sum \frac{C_i}{C_s}$ = the sum of all the concentration ratios determined determined from the individual analytical curves, and, as before, and
- T = the concentration assumed for the total of all the trace elements not measured.

The concentration of the internal standard can be calculated from Eq 6 as:

$$C_s = \frac{100 - T}{1 + \sum \frac{C_i}{C_s}} \quad (7)$$

7.2.2 The concentration ratio method requires that all elements be measured if they are likely to occur in concentrations above 0.3 %. If the total of the trace elements not measured is not likely to exceed 0.5 % and if the total is not expected to vary by more than 0.1 %, T can either be represented by the probable total as a constant, or the term can be disregarded, without affecting any measurement significantly except the concentration of the internal standard.

7.2.3 Once the concentration for the internal standard has been calculated, the other concentrations can be computed by:

$$C_i = \left(\frac{C_i}{C_s} \right) C_s \quad (8)$$

NOTE 1—Coulliette originally included the concentration ratio method of calculation as Section 9 in previous editions of Practice E 158, but it was never used extensively either in photographic or direct-reading analysis because reading the concentration ratios from the curves, and making the calculations added substantially to the time of analysis. However, with the introduction of programmable calculators or computers, the calculations became practicable.

8. Background Correction

8.1 *Utility*—Background correction is appropriate only when working close to the detection limit. Then it offers the following advantages:

8.1.1 On a log-log plot, background correction will extend the straight-line response to lower concentrations. The apparent improved response provides better readability. If the same

data are plotted linearly there will be no benefit; the curve will merely be moved down toward the origin.

8.1.2 If the background under an analytical line increases proportionally to a matrix element, background correction can improve the accuracy of analysis.

8.1.3 If the background varies significantly from exposure to exposure, independently of the line signal or overall exposure, background correction can improve the precision and accuracy of the analysis and thus can improve the detection limit.

8.1.4 In a direct reader, background correction may make it possible to read concentrations directly, as explained later.

8.1.5 These benefits become real only if the instrument or the analytical procedure, or both, can produce good long-term stability.

8.2 *Photographic Background Correction*—On a photographic plate or film, it is easy to measure the background beside a line and to ensure that this measurement does not include lines of possible interfering elements. The approved method of background correction recognizes and compensates for the emulsion's logarithmic response. This involves a rather complicated and lengthy procedure which is described in detail in Practice E 116E 116. Such corrections have been used to improve the detection limits of trace elements in uranium.

8.3 *Background Correction with Direct Readers*—At low concentrations, a direct reader gives an overall reading that is largely background and partly signal, but there is no simple means of distinguishing which is which. On the other hand, because of the linear response of photomultipliers, at low concentrations both the line signal and the background respond linearly, so that background correction can be done more simply than photographically. It consists of a simple subtraction. Three methods of background correction are employed:

8.3.1 With static background correction, a fixed number is subtracted from all readings. For example, for the data of Table 1, 0.025 might be subtracted from all of the readings of Column 4. If negative readings are considered objectionable, subtract slightly less than the full background reading of 0.030, because otherwise some negative readings will be obtained as a result of statistical fluctuations in the data. Alternatively, if a computer is being used, the full background correction can be applied, and the software can be written either to instruct the computer to print a zero instead of a negative intensity ratio, or to indicate that the reading falls below the lowest meaningful intensity ratio.

8.3.2 With dynamic background correction, the background is measured in each exposure by one or more exit slits, which are profiled to make sure that they show no line response to any of the elements in the matrix. A portion of the background reading is subtracted from an analytical channel to obtain a net figure for the line itself. For example, a background slit might read 0.150. For the data in Table 1, a potentiometer or other control would be adjusted to deduct 0.025 to 0.029 from the analytical channel. The full correction of 0.030 can be avoided if desired, to prevent frequent negative readings. With a computer readout, a correction factor for the background can be selected to apply a similar correction. Also with a computer readout, negative numbers can be avoided.