Designation: E 1622 – 94 (Reapproved 1999)[ε1]

Standard Practice for
Correction of Spectral Line Overlap in Wavelength-Dispersive X-Ray Spectrometry[1]

This standard is issued under the fixed designation E 1622; 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.

ε[1] NOTE—The jurisdiction of this practice was changed from Subcommittee E01.22 to E01.20.

1. Scope

1.1 Procedures are given for the correction of line overlap interferences encountered in the analysis of metallic and nonmetallic specimens in wavelength dispersive X-ray spectrometry.

1.2 Spectral interference occurs when a line of another element appears at or close to the same wavelength as the analyte line. The interfering line or lines may be from the same spectral order as the analyte line or may be from another spectral order. Line overlap interferences from higher order lines are usually removed when pulse-height discrimination is used.

1.3 The procedures given in this practice are applicable to making corrections for interferences arising from concomitants in the sample. Interfering lines from the X-ray tube and associated instrumental components are usually specific to the system and the procedure for dealing with these may be found elsewhere. This is treated by E. P. Bertin.[2]

1.4 This practice is not generally applicable to simultaneous X-ray spectrometers if it is not possible to measure a line of the interfering element. Correction is possible, however, if the concentration of the interfering element is known and can be entered into the analytical program.

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 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[3]
E 1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis[4]

3. Terminology

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

4. Significance and Use

4.1 To make accurate analytical determinations, the contribution of an unresolved line or lines to the measured intensity of an analyte must be subtracted before calculating its concentration. A correction factor determined by using this practice permits a calculation of the amount to subtract from X-ray spectrometric data to eliminate the portion of a signal that is due to line interference.

4.2 The methods described in 5.1.1 and 5.1.2 may not be applicable if there are severe matrix effects that change the intensity ratio between the interfering line and another line of the same element. For example, with reference to Fig. 1, if there is an absorption edge of another element between P_1 and P_2, correction for an absorption effect may be required. See Guide E 1361.

4.3 Correcting for line overlap requires relatively precise measurements to avoid inaccuracy from accumulated imprecisions (see 6.1.). Choose a counting time that reduces imprecision to an acceptable level. Counting error is equal to $\sqrt{N}$, and the relative error is equal to $\sqrt{N}/N$ or $\sqrt{1/N}$, where N is the total number of counts. If measurements are taken in counts per second, using R to designate this rate, the relative error is equal to $\sqrt{R}/(R\sqrt{T})$ or $\sqrt{1/RT}$, where T is the length of time taken for the measurement. Relative error, therefore, is reduced by increasing the measurement time, which also increases total counts.

4.3.1 Since background correction is needed to determine net counts or net count rates, uncertainty in the background reading contributes to the imprecision in the net count or net count rate. The standard deviation of a net reading, S_N, is the root mean square of the standard deviations of the peak and the background reading, σ_P and σ_B, respectively, or $\sqrt{\sigma_P{}^2 + \sigma_B{}^2}$. Variance, however, is equal to counts, which
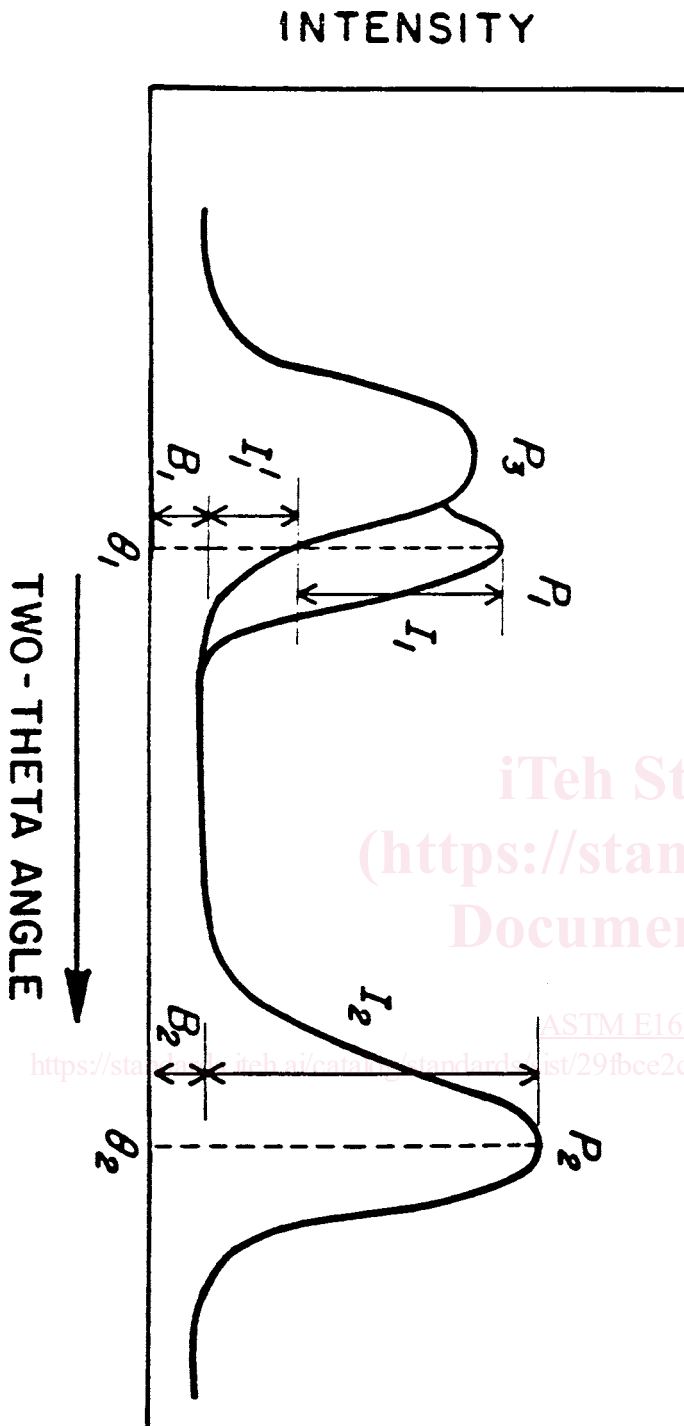

INTENSITY

FIG. 1 Typical Line Overlap

makes $\sigma_N = \sqrt{N_P + N_B}$. Relative error of the net signal, ϵ_N, therefore is equal to $\sqrt{N_P + N_B}/(N_P - N_B)$. By recognizing that background counts are some fractional part of peak counts, ϵ_N can be seen to be equal to $\sqrt{N_P + bN_P}/(N_P - bN_P)$, where b is the fractional factor. The N_P component can then be factored out of the expression to make $\epsilon_N = \sqrt{1/N_P}[\sqrt{1 + b}/(1 - b)]$. In a similar fashion, ϵ_N can be seen to be equal to $\sqrt{1/R_N T}[\sqrt{1 + b}/(1 - b)]$, when readings are taken in terms of counts per second and R_N is the count rate observed over T seconds. In either measurement

system, the factor causing an increase in imprecision is $\sqrt{1 + b}/(1 - b)$. It can then be seen that if background is 40 % of the peak reading, the imprecision of the net reading will be increased by almost two-fold.

4.4 The following methods of correction are based on intensities in terms of total counts. The equations may also be used for intensities in terms of count rates. If total counts are used, it is imperative that the counting time for any one intensity reading is not changed, since such a change would invalidate the correcting factor being used.

5. Methods of Correction

5.1 When the measured intensity of an analyte includes counts from an interfering line, the contribution of the interference may be inferred and eliminated by measuring another line of the interfering element. The alternate line, however, must be free of interferences. In Fig. 1, P_1 is the analyte line that is being measured at the angular position Θ_1, P_3 is an interfering line which contributes some of its intensity to P_1. P_2 is another line of the interfering element appearing at angular position Θ_2. The observed measurement is:

$$I_{\Theta 1} = I_1 + I'_1 + B_1 \tag{1}$$

where:
$I_{\Theta 1}$ = total intensity, in counts, measured at Θ_1,
I_1 = net intensity, in counts, of the analyte at Θ_1,
I'_1 = net contribution, in counts, of the interfering line, P_3, appearing at Θ_1, and
B_1 = intensity, in counts, of the background at Θ_1.

5.1.1 *Use of Pure Elements*—Determine a factor, F, relating the relative intensity of the overlapping line at Θ_1 to another line, P_2, of the same interfering element at Θ_2 by using a pure specimen of the interfering element. The specimen may be a metal foil or an oxide powder. Correcting all measurements for background, the determination is as follows:

$$F = I'_1/I_2 \tag{2}$$

where:
I_2 = net intensity, in counts, of the fully resolved line, P_2, of the interfering element measured at Θ_2, $(I_{\Theta 2} - B_2)$, where B_2 is the intensity in counts, of the background at Θ_2.

5.1.1.1 Calculate the corrected net intensity of the analyte using:

$$I_1 = I_{\Theta 1} = B_1 = F(I_2) \tag{3}$$

NOTE 1—When measuring pure elements it is important to verify that the count rate does not exceed the linearity of the detection system. A plot of count versus tube current will establish the limit of linearity. If bending is observed, the X-ray power must be reduced. The reduction can be done by reducing the current of the X-ray tube, but do not reduce the voltage applied to the X-ray tube.

5.1.2 *Use of Synthetic Specimens*—Prepare specimens containing increasing amounts of the interfering element. The contribution of the interfering element to the intensity of the analytical wavelength can be established graphically. The net intensity, the reading corrected for background, measured at the analytical wavelength is plotted against the net intensity measured for a line of the interfering element that is free of