



# Standard Practice for Correction of Spectral Line Overlap in Wavelength- Dispersive X-Ray Spectrometry<sup>1</sup>

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.

<sup>ε1</sup> 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.<sup>2</sup>

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<sup>3</sup>

E 1361 Guide for Correction of Interelement Effects in

## X-Ray Spectrometric Analysis<sup>4</sup>

## 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,  $\sigma_P$  and  $\sigma_B$ , respectively, or  $\sqrt{\sigma_P^2 + \sigma_B^2}$ . Variance, however, is equal to counts, which makes  $\sigma_N = \sqrt{N_P + N_B}$ . Relative error of the net signal,  $\epsilon$

<sup>1</sup> 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 E01.20 on Fundamental Practices and Measurement Traceability. Current edition approved July 15, 1994. Published September 1994.

<sup>2</sup> Bertin, E. P., *Principles and Practice of X-Ray Spectrometric Analysis*, Plenum Press, New York, NY, Second edition, 1975, p. 553.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.06.

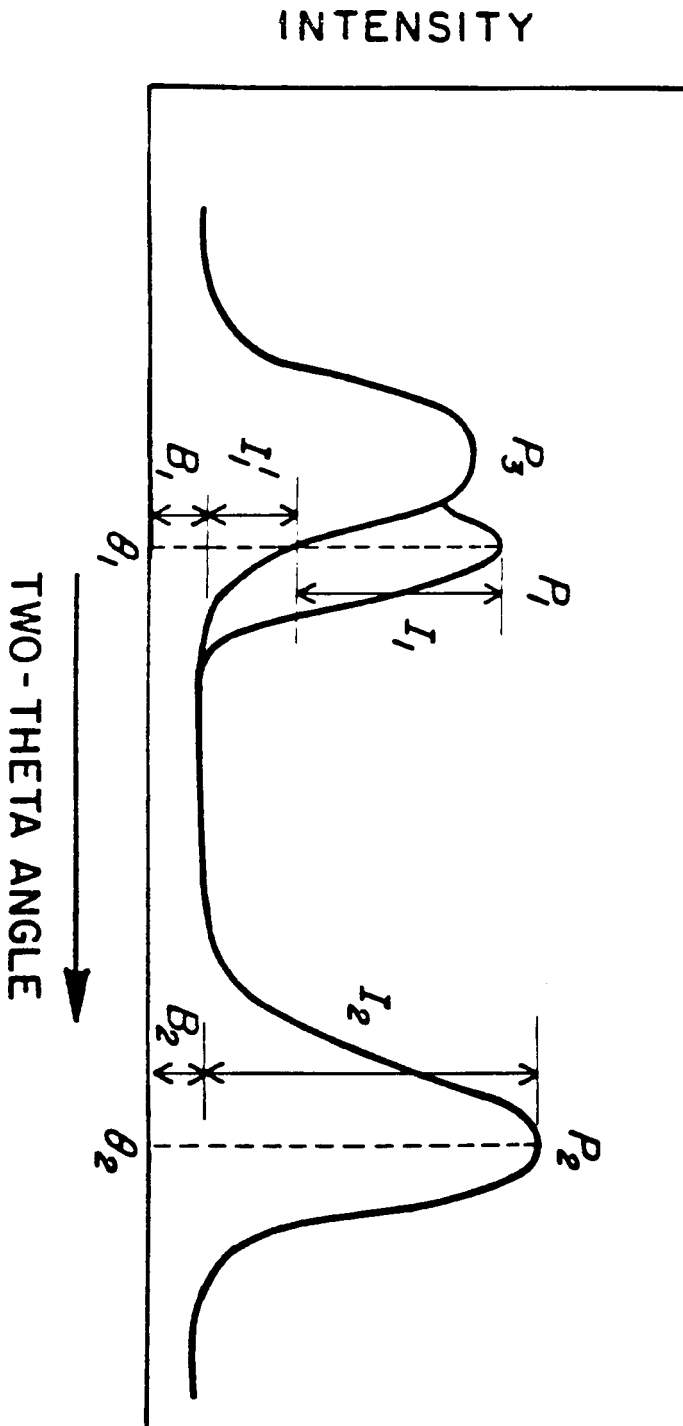


FIG. 1 Typical Line Overlap

$N$ , 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,  $\epsilon_N$  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,  $\epsilon_N$  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  $\Theta_1$ ,  $P_3$  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  $\Theta_2$ . The observed measurement is:

$$I_{\Theta_1} = I_1 + I'_1 + B_1 \quad (1)$$

where:

- $I_{\Theta_1}$  = total intensity, in counts, measured at  $\Theta_1$ ,
- $I_1$  = net intensity, in counts, of the analyte at  $\Theta_1$ ,
- $I'_1$  = net contribution, in counts, of the interfering line,  $P_3$ , appearing at  $\Theta_1$ , and
- $B_1$  = intensity, in counts, of the background at  $\Theta_1$ .

5.1.1 *Use of Pure Elements*—Determine a factor,  $F$ , relating the relative intensity of the overlapping line at  $\Theta_1$  to another line,  $P_2$ , of the same interfering element at  $\Theta_2$  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:

$$F = I'_1/I_2 \quad (2)$$

where:

- $I_2$  = net intensity, in counts, of the fully resolved line,  $P_2$ , of the interfering element measured at  $\Theta_2$ ,  $(I_{\Theta_2} - B_2)$ , where  $B_2$  is the intensity in counts, of the background at  $\Theta_2$ .

5.1.1.1 Calculate the corrected net intensity of the analyte using:

$$I_1 = I_{\Theta_1} - B_1 = F(I_2) \quad (3)$$

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 interference. The slope will be equal to the overlap correction factor,  $F$ , in Eq 2. See Fig. 2.