Designation: E 1622 – 94 (Reapproved 1999)$^{\epsilon 1}$

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 makes $\sigma_N = \sqrt{N_P + N_B}$. Relative error of the net signal, ϵ

[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 E01.20 on Fundamental Practices and Measurement Traceability.

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

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

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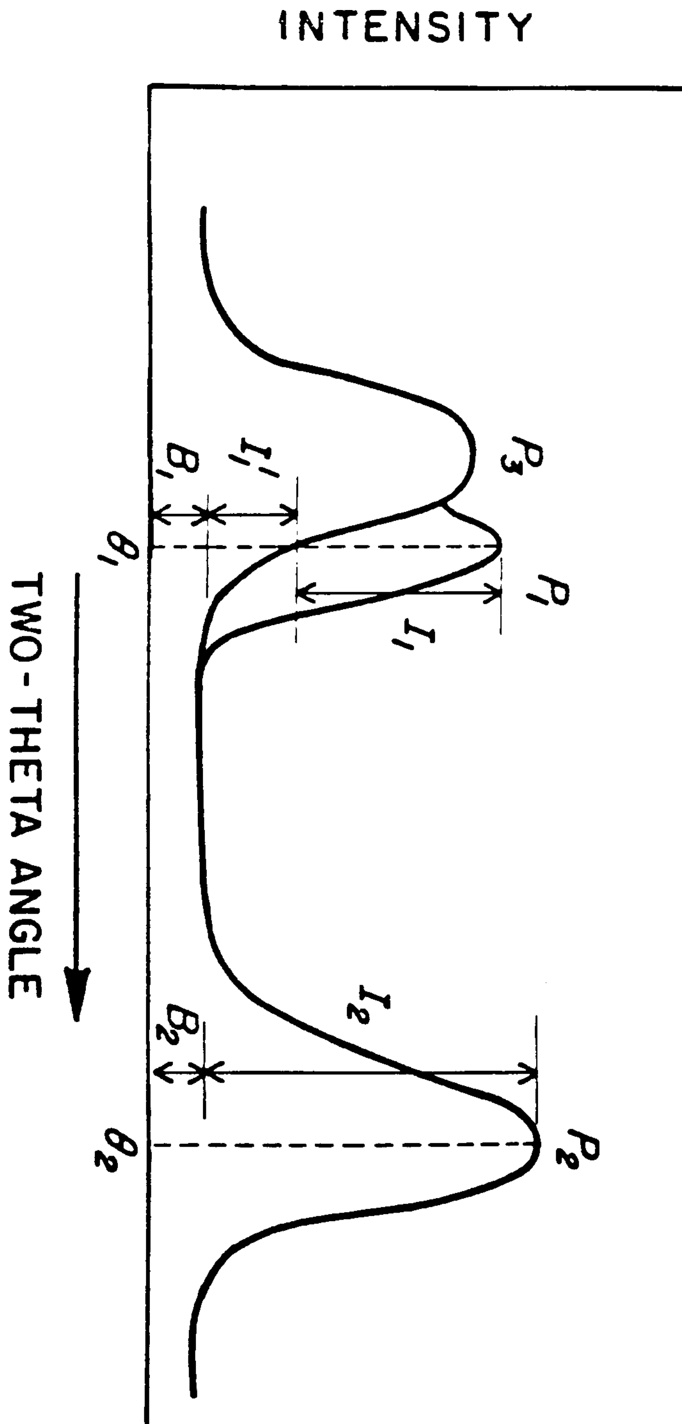

FIG. 1 Typical Line Overlap

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

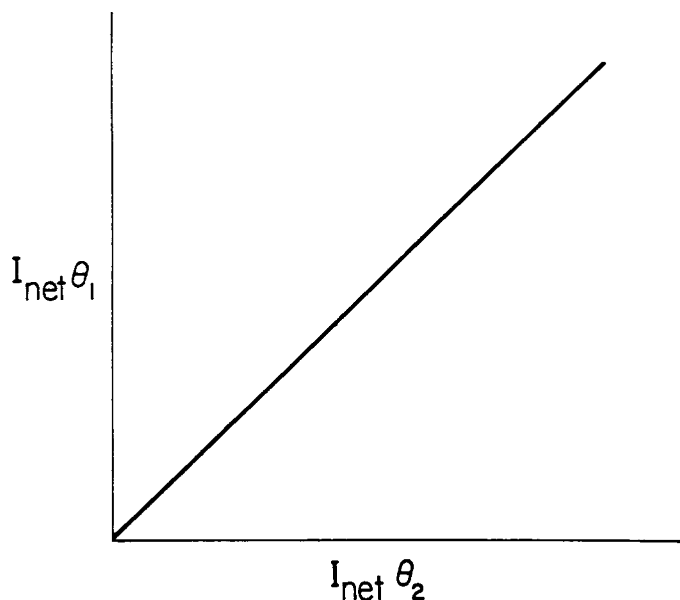

FIG. 2 Typical Plot of Interference to Another Measurement of the Interfering Line

5.1.3 *Use of Regression Analysis*—Frequently it is not possible to prepare specimens specifically for the determination of line overlap correction factors. It is possible, however, to use a series of specimens with varying amounts of both the analyte and the interfering element to determine the overlap correction factor through the use of multiple linear regression using the following relationship:

$$C = a_0 + a_1 I_n + a_2 I_2 \quad (4)$$

where:

C = concentration of the analyte,
a_0 = a constant,
I_n = $I_1 + I'_1$ net counts measure at the analyte wavelength, unresolved peak (see Fig. 1), and
I_2 = net counts of the interfering element, measured at another wavelength which is interference free.

NOTE 2—Concentration may be used instead of net count intensity for I_2 in Eq 4.

5.1.3.1 Eq 4 can be rearranged as follows:

$$C = a_0 + a_1[I_n + (a_2/a_1)I_2] \quad (5)$$

where:

a_2/a_1 = line overlap correction factor, which should be negative.

5.1.3.2 When I_n, I_2, and C are known for a series of specimens, the constants a_0, a_1, and a_2 in Eq 4 may be calculated by multiple linear regression as described in texts on statistics,[5,6] or by use of a computer program (Note 3). In this case, two regressions on the concentration variable are determined: the primary relationship to the intensity measured at the analyte wavelength; and a secondary relationship to an intensity measured for another reading of the interfering element. The line correction factor a_2/a_1 is calculated and substituted for F in Eq 3, after changing its sign. The computer program used for the X-ray spectrometer may permit a regression to determine the correction factor.

NOTE 3—Standard spreadsheet programs often are able to determine regression coefficients.

NOTE 4—The value of the constant, a_0, is an indication of how well the background correction has been performed. Ideally, a_0 should be equal to zero. Small positive values indicate residual background. If a large value is obtained a gross error has been committed in performing the background correction. If a simultaneous spectrometer is used, a_0 would be equal to the background, not to zero.

NOTE 5—Experience has shown that this method requires a large spread in the range of analyte and interfering elements in the standards. For the three constants that must be determined, it is advisable to have a suite of at least ten specimens.

6. Comments

6.1 Whenever an observed measurement is corrected by other measurements, the standard deviation of the corrected measurement is the square root of the sum of the variances of the individual measurements, weighted by how they are used. In Eq 3, the standard deviation of the corrected line is:

$$s = \sqrt{s_t^2 + s_{b1}^2 + F(s_i + s_{b2}^2)} \quad (6)$$

where:

s_t^2 = variance of the total measurement, $I_{\Theta 1}$,
s_{b1}^2 = variance of the background measurement, B_1,
s_i^2 = variance of the total measurement of the interfering line, I_2, and
s_{b2}^2 = variance of the background measurement, B_2.

6.1.1 Variation in the factor F will not significantly affect the standard deviation of the corrected line. A poor definition of F, however, will bias the corrected line measurement.

6.1.2 An example of a calculation of the imprecision of a corrected count appears in the Appendix.

7. Keywords

7.1 interferences; line overlap; precision; wavelength dispersive X-ray spectrometry

[5] Box, G. E. P., Hunter, W. G., and Hunter, J. S., *Statistics for Experimenters, Wiley Series in Probability and Mathematical Statistics*, John Wiley & Sons, New York, NY, pp. 453–509.

[6] Montgomery, D. C., and Peck, E. A., *Introduction to Linear Regression Analysis, Wiley Series in Probability and Mathematical Statistics* , John Wiley & Sons, New York, NY, pp. 109–180.

APPENDIXES

(Nonmandatory Information)

X1. EXAMPLES

X1.1 *Application of the Use of Pure Elements*—Molybdenum L_α interferes with sulfur K_α, measured at 75.85°, in the determination of sulfur in low alloy steels, using a PET (002) crystal.

X1.1.1 Using molybdenum foil, measure 471 530 counts as the total signal at 75.85°. Measure 20 152 counts as the background at 73.65°. The net intensity of the interfering line is as follows:

$$I_1' = 471\,530 - 20\,152 = 451\,378 \quad \text{(X1.1)}$$

X1.1.2 Measure 1 017 486 counts as the total signal for the molybdenum L_β at 72.63°. Measure 29 302 counts as the background at 71.73°. The net intensity of the molybdenum L_β line is:

$$I_2 = 1\,017\,486 - 29\,302 = 988\,184 \quad \text{(X1.2)}$$

NOTE X1.1—The example in X1.1.2 uses total counts. If count rate were being used, the large numbers shown would represent an excessive drive on a detector that would force it out of a linear response.

X1.1.3 Calculate the overlap factor, *F*, using Eq 2:

$$F = 451\,378/988\,184 = 0.4568 \quad \text{(X1.3)}$$

X1.1.4 Analyze a specimen containing molybdenum and sulfur, measuring $I_{\Theta 1}$ = 606 counts for the total signal for sulfur K_α and 196 counts for the nearby background.

X1.1.5 Measure 846 counts for the total signal for molybdenum *L*, and 234 counts for the nearby background. The net intensity of the reference interfering line is as follows:

$$I_2 = 846 - 234 = 612 \quad \text{(X1.4)}$$

X1.1.6 Calculate the corrected intensity of the analyte, using Eq 3:

$$I_1 = 606 - 196 - 0.4568(612) = 130 \quad \text{(X1.5)}$$

X1.1.7 See Appendix X2 for a calculation of the precision of the final, corrected count.

X1.2 *Application of Use of Synthetic Specimens*—Lead L_α interferes with arsenic K_α at 48.83° in the determination of arsenic in lead ores, using a LiF (220) crystal.

X1.2.1 Prepare a series of specimens by adding a lead compound to a suitable matrix.

X1.2.2 Measure the total signal at 48.83° and the background at 50.0°. Measure the total signal for the lead L_β line at 40.38° and the background at 41.0°.

X1.2.3 Table X1.1 represents a set of X-ray intensity measurements at various wavelengths.

X1.2.4 Use the data in Table X1.1 to plot a graph of the net intensity at the arsenic K_α line at 48.83° against the net intensity at the lead L_β line at 40.38°. The plot should pass through the point (0,0). See Fig. X1.1.

X1.2.5 The slope is equal to the line overlap-correction factor, *F*, in Eq 2.

TABLE X1.1 Measurements for Applying Synthetic Specimens

Pb, %	As K_α [A]	Pb L_β [A]
5.0	5552	6761
2.5	2776	3381
1.25	1388	1690
0.625	694	845

[A] Total counts corrected for background.

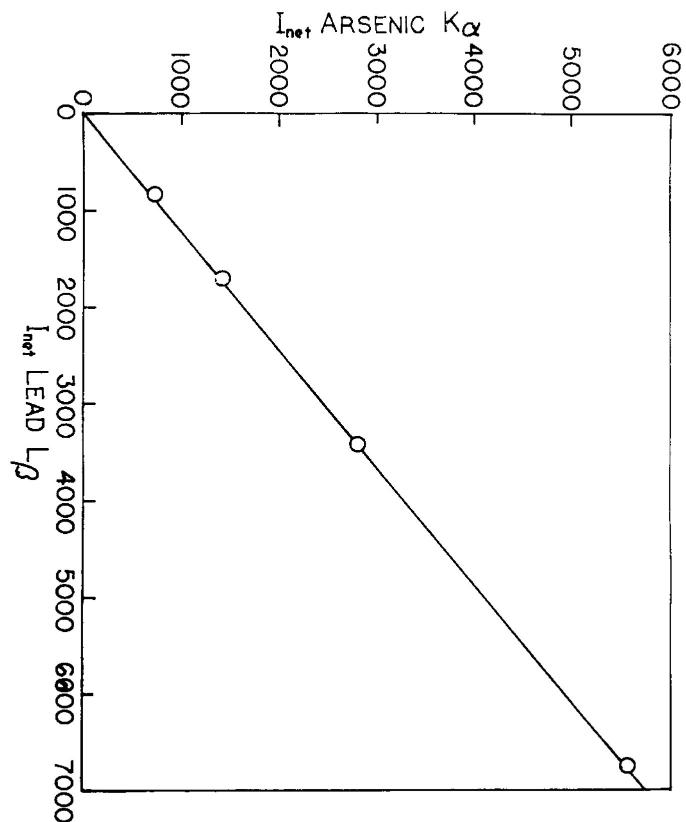

FIG. X1.1 Interference of Lead L_a on the Arsenic K_α Measurement as a Function of the Lead L_β Signal

X1.3 *Application of Use of Regression Analysis*—Chromium K_β interferes with manganese K_α, measured at 63.06°, in the determination of manganese in stainless steel containing high chromium, using a LiF (200) crystal.

X1.3.1 Using a series of stainless steel standards, measure the total signal for manganese at 63.06° and the background at 64.0°. Measure the total signal for chromium K_α at 69.37° and the background at 70.0°.

X1.3.2 Table X1.2 represents a set of X-ray intensity measurements at various wavelengths.

X1.3.3 Use the data in Table X1.2 to define a series of simultaneous equations (see Eq 4) to calculate the following coefficients using multiple linear regression:

TABLE X1.2 Measurements for Applying Regression Analysis[A]

Reference Material[B]	I_n Mn K_α[C]	I_2 Cr K_α[C]	C Mn, %
SS-61	1754	103 748	0.78
SS-62	1746	86 954	0.80
SS-63	1803	119 732	0.79
SS-64	2004	146 308	0.85
SS-65	2068	115 766	0.94
SS-66	1749	106 064	0.81
SS-67	1926	112 152	0.87
SS-68	3369	117 777	1.59
SS-69	980	90 378	0.41
SS-70	970	113 101	0.38
SS-71	1115	151 066	0.43
SS-72	2014	107 738	0.91

[A] Data obtained on a Philips Electronic Instruments spectrometer.
[B] British analyzed austenitic and martensitic stainless steels.
[C] Total counts corrected for background.

$$a_0 = 0.01937, \tag{X1.6}$$

$$a_1 = 5.0305 \times 10^{-4}, \text{ and}$$

$$a_2 = -1.0848 \times 10^{-6}.$$

The line overlap factor, $a_2/a_1 = -2.1564 \times 10^{-3}$.

X2. AFFECT OF LINE OVERLAP CORRECTION ON PRECISION

X2.1 In 6.1, Eq 6 states how to calculate the standard deviation of the count for a line that has been corrected for overlap. Following is a determination of that measurement for the example that appears in X1.1.

X2.2 The imprecision of four measurements determines the overall calculation of a standard deviation, namely the total count for the uncorrected sulfur reading and the count for its background, which appears in X1.1.6, and the total count for a molybdenum line and the count for its background, which appears in X1.1.5. A factor of 0.4568 was determined in X1.1.3 for relating how much of this molybdenum count could be ascribed to being an overlap on the sulfur line.

X2.3 Noting, as stated in 4.3.1, that variance of an X-ray count is equal to that count, the relationship of Eq 6 can be restated as being:

$$s^2 = N_t + N_{b1} + F(N_i + N_{b2}) \tag{X2.1}$$

where:

N_t = count of the total measurement, $I_{\Theta 1}$,
N_{b1} = count of the background measurement, B_1,
N_i = count of the total measurement of the interfering line, I_2, and
N_{b2} = count of the background measurement, B_2.

X2.3.1 Using the example values appearing in X1.1.6, for the analyte, sulfur, $I_{\Theta 1}$ = 606, and its background, B_1, = 196.

X2.3.2 Using the example values appearing in X1.1.5, for the interfering element, Mo, I_2 = 846, and its background, B_2 = 234.

X2.3.3 Using the value of 0.4568 for F, as calculated in X1.1.3, the sum of the variance of the corrected sulfur signal is as follows:

$$s^2 = 606 + 196 + 0.4568(846 + 234) \tag{X2.2}$$

$$= 802 + 0.4568(1080) = 1295$$

$$s = 36$$

Therefore:

X2.3.4 With the corrected measurement equal to 130, as calculated in X1.1.6, the relative standard deviation of the corrected measurement is:

$$RSD = 100(36/130) = 28\ \% \tag{X2.3}$$

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