



## Practice for Performance-Based Description of Instruments in Chemical Analysis Methods<sup>1</sup>

This standard is issued under the fixed designation E 2054; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This practice covers procedures for specifying instruments for chemical analysis by performance rather than by design.

1.2 The provisions of this practice do not apply to classical chemical method of analysis.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>2</sup>

E 396 Test Method for Chemical Analysis of Cadmium<sup>3</sup>

E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry<sup>3</sup>

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method<sup>3</sup>

E 1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods<sup>3</sup>

E 1914 Practice for the Use of Terms Relating to the Development and Evaluation of Methods of Chemical Analysis<sup>3</sup>

E 2055 Practice for Referencing Methods for Chemical Analysis of Metals and Related Materials<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For definitions and use of terms used in this practice, refer to Terminology E 135 and Practice E 1914.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *classical analytical method, n*—a method based upon classical analytical measurements, that is, weight (as by analytical balance), volume (as by buret), or both.

3.2.2 *instrumental analytical method, n*—a method based upon analytical measurements other than those employed in classical methods.

3.2.3 *minimum instrument sensitivity index, MISI, n*—a

figure of merit used to compare sensitivity of instruments at low analyte levels.

3.2.4 *relative instrument sensitivity index, RISI, n*—a figure of merit used to compare sensitivity of instruments at elevated analyte levels.

### 4. Summary of Practice

4.1 The author or a task group conducting an interlaboratory study (ILS) examines a measuring instrument to determine which components and operations contribute to imprecision of results. The task group collects ILS data and calculates values for criteria that define acceptable operation of those components. Instrument tests and critical values are written into the Apparatus section. Before applying a method, users verify that an instrument meets the specified performance criteria.

### 5. Significance and Use

5.1 Instrumental methods specify measurement apparatus by name and a brief design description. An instrument designed differently than described may provide equivalent measurements. Relying solely on design specifications sometimes excludes instruments capable of the required performance.

5.2 This practice requires each method to specify tests and criteria to measure critical performance characteristics of an instrument. The tests provide verification that a user's instrument is capable of producing results that reflect the precision stated in the method.

5.3 Any instrument designed to measure the physical properties in the specified analytical systems may be used in a method if it meets the performance criteria. If an instrument's performance does not meet the criteria, a user may still apply the method, but is warned that results may have greater variability than is specified in the method. (**Warning**—Meeting instrument performance criteria does not guarantee expected precision and accuracy. The tests warn only of excessive instrumental error. A user shall employ reference materials in accordance with Practice E 2055 and adhere strictly to all requirements of a method to obtain results in accordance with its Precision and Bias section.

5.4 Classical analytical methods are not covered by this practice.

<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 E01.22 on Statistics and Quality Control.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.06.

## 6. Minimum Performance Parameters

6.1 In instrumental methods, results are calculated from an instrument's response to an analyte's concentration. Readings are visually estimated values from an instrument's analog scale or digital values derived mechanically or electronically from its output. A method specifies manual calculation of results from instrument readings or programmed calculation by a computer. Some instruments may be calibrated to provide readings directly in analyte content or concentration. In any case, a method specifies one instrument sensitivity index near the bottom and another near the top of an analyte's calibrated range. The associated performance tests, conditions, and criteria constitute minimum performance requirements for an instrument.

## 7. Instrument Tests

7.1 *Instrument Test Protocols*—Instrument performance tests are devised by the author or a task group before ILS testing is begun. The statistical criteria for the tests are calculated from the normal ILS statistics or from data collected separately as part of the ILS experiment.

7.1.1 *Sensitivity Tests*—All methods require sensitivity tests at two analyte levels, one near the low end (MISI) and the other near the high end (RISI) of a calibration range. Identify the two test solutions or specimens in sufficient detail that users perform the tests on appropriate samples. For flame atomic absorption (FAA) methods, for example, specify the zero and highest calibration solutions for determination of MISI and RISI, respectively. Provide instructions for the performance tests in the Apparatus section of the method. Sensitivity tests under this practice require 10 sequential readings on each test material. For FAA methods, for example, the sensitivity test might read: "Prepare the instrument for measurements on the analyte in accordance with manufacturer's recommendations, and calibrate according to Section \_\_\_\_\_. Take 10 sequential readings on the zero calibration solution and 10 on the highest calibration solution, and calculate the sample standard deviations  $s_0$  and  $s_H$ , respectively. Calculate the relative standard deviation:

$$s_{rel} = s_H/\bar{x}_H \quad (1)$$

where  $\bar{x}_H$  is the mean of the 10 high material readings. If  $s_0$  is less than [insert value of  $I_0$ ], the instrument has satisfactory low-level sensitivity. If  $s_{rel}$  is less than [insert value of  $I_{rel}$ ], the instrument has satisfactory high-level sensitivity. If either statistic frequently exceeds its index value, the instrument may contribute excessive variability in the corresponding calibration region."

7.1.2 *Special Tests*—Add tests of other instrument parameters, if appropriate (see Annex A2). For FAA, for example, begin instrument testing with a response linearity test in accordance with A2.3.

7.2 *Instrument Test Criteria*—The task group uses the ILS test data to calculate critical values for the acceptance statistics established in 7.1.

7.2.1 *Instrument Sensitivity Indexes*—Prepare a table of means,  $\bar{x}$ , minimum method standard deviations,  $s_M$ , and other statistics as shown for the example in Table 1 in which each laboratory provided 3 results. Calculate relative values for  $s_M$ :

**TABLE 1 Sensitivity Statistics for Copper in Iron Ore**

Material	Mean, $\bar{x}$	$s_M$	$s_{rel}$	$p$	$f$
1	0.001	0.0003	0.30	35	70
2	0.011	0.0007	0.064	39	78
3	0.072	0.0013	0.0181	39	78
4	0.380	0.0059	0.0155	40	80
5	0.787	0.0115	0.0146	40	80

$$s_{rel} = s_M/\bar{x} \quad (2)$$

Calculate the degrees of freedom:

$$f = p \times (n - 1) \quad (3)$$

where:

$p$  = the number of laboratories contributing data, and

$n$  = the number of replicates from each laboratory.

From Annex A1, select a procedure for determining the low-analyte sensitivity constant,  $k_0$ , high-analyte constant,  $k_{rel}$ , and their associated degrees of freedom,  $f_0$  and  $f_{rel}$ . Determine the corresponding factors,  $F_0$  and  $F_{rel}$  from Table 2. Calculate critical index values for MISI and RISI:

$$I_0 = \sqrt{k_0^2 \times F_0} \quad (4)$$

$$I_{rel} = \sqrt{k_{rel}^2 \times F_{rel}} \quad (5)$$

Enter the critical values in the method's test protocol.

7.2.2 *Example for Copper in Iron Ore by FAA*—The ILS statistics for this method are shown in Table 1. By inspection,  $k_0 = 0.0003$  with  $f_0 = 70$  ( $F_0 = 2.0$ ) and  $k_{rel} = 0.0150$  with  $f_{rel} = 160$  ( $F_{rel} = 1.9$ ). From Eq 4,  $I_0 = 0.00042$ ; from Eq 5,  $I_{rel} = 0.021$ . The sensitivity test might read: Prepare the instrument to measure copper in accordance with the manufacturer's recommendations, and calibrate according to Section \_\_\_\_\_. Record 10 sequential copper results for the zero calibration solution and 10 for the highest calibration solution and calculate their sample standard deviations  $s_0$  and  $s_H$ , respectively. Calculate the relative standard deviation,  $s_{rel}$ :

$$s_{rel} = s_H/\bar{x}_H \quad (6)$$

where  $\bar{x}_H$  is the mean for the highest calibration solution. If  $s_0$  is less than 0.00042 % copper, the instrument has satisfactory low-level sensitivity. If  $s_{rel}$  is less than 2.1 %, the instrument has satisfactory high-level sensitivity. If either statistic frequently exceeds its index value, the instrument may contribute to excessive variability in the corresponding calibration region.

**TABLE 2 F Factor**

$f$ Range	$F$
11	2.9
12	2.8
13–14	2.7
15	2.6
16–18	2.5
19–21	2.4
22–27	2.3
28–36	2.2
37–58	2.1
59–120	2.0
> 120	1.9

## ANNEXES

### (Mandatory Information)

#### A1. SENSITIVITY CONSTANTS $k_0$ AND $k_{rel}$

**A1.1 Precision Models**—Refer to Guide E 1763 for a general discussion of models for the precision of methods of chemical analysis. Guide E 1763 deals exclusively with repeatability and reproducibility, but the same principles apply to relationships between analyte concentrations and minimum method standard deviations,  $s_M$ . One of the procedures outlined in this annex provides a means to estimate the low-level sensitivity constant,  $k_0$ , and the high-level constant,  $k_{rel}$ .

**A1.2 Case 1: Limited Test Materials**—If the ILS is conducted with a limited number of test materials, or if the analyte content of one or more materials is nearly zero, set  $k_0$  equal to  $s_M$  of the test material with lowest analyte content or the pooled value of  $n$  low materials with about the same  $s_M$ . Calculate  $f_0$  for the low material for  $s_M$ . Degrees of freedom for an individual material,  $i$ , is  $f_i = p \times (n - 1)$ , where  $p$  laboratories contribute  $n$  replicate results for the material. For data pooled over  $q$  low materials 1, 2, ...,  $q$ , the equations for pooled  $k_0$  and pooled  $f_0$  become:

$$k_0^2 = \frac{(f_1)(s_M)_1^2 + (f_2)(s_M)_2^2 + \dots + (f_q)(s_M)_q^2}{f_1 + f_2 + \dots + f_q} \quad (\text{A1.1})$$

$$f_0 = f_1 + f_2 + \dots + f_q \quad (\text{A1.2})$$

Set  $k_{rel}$  equal to  $s_{rel}$  of the test highest material or to the pooled value of  $m$  high materials having nearly the same  $s_{rel}$ .

For pooled high analyte materials 1, 2, ...,  $m$ , the equations for pooled  $k_{rel}$  and pooled  $f_{rel}$  become:

$$k_{rel}^2 = \frac{(f_{rel})_1(s_{rel})_1^2 + (f_{rel})_2(s_{rel})_2^2 + \dots + (f_{rel})_m(s_{rel})_m^2}{(f_{rel})_1 + (f_{rel})_2 + \dots + (f_{rel})_m} \quad (\text{A1.3})$$

$$f_{rel} = (f_{rel})_1 + (f_{rel})_2 + \dots + (f_{rel})_m \quad (\text{A1.4})$$

**A1.3 Case 1 Example**—The plot of  $s_M$  against copper content in Fig. A1.1 suggests that, in the ILS of the method for copper in iron ore by FAA (data from Table 1 in the practice), only the lowest test material estimates a constant value for  $s_M$ . Thus the estimate of  $k_0$  is 0.0003 with  $f_0 = 70$ . In Table 1, materials 4 and 5 exhibit nearly a constant value for  $s_{rel}$ . Applying Eq A1.1 and A1.2 yields pooled values of  $k_{rel} = 0.015$  and  $f_{rel} = 160$ . These values of  $k_0$ ,  $f_0$ ,  $k_{rel}$ , and  $f_{rel}$  appear in the calculations of sensitivity indexes in 7.2.1.

**A1.4 Case 2: Many Test Materials**—If the ILS is conducted with materials at many different analyte concentrations,  $C_1 \dots C_m$ , the precision model may be applied. From the  $m$  data pairs  $(s_M, C)$  obtained in the ILS, calculate constants  $k_0$  and  $k_{rel}$  in accordance with procedures in Annex A2 of E 1763. The curve-fit process must be performed with a general non-linear procedure or special least-squares algorithms to accommodate the model:

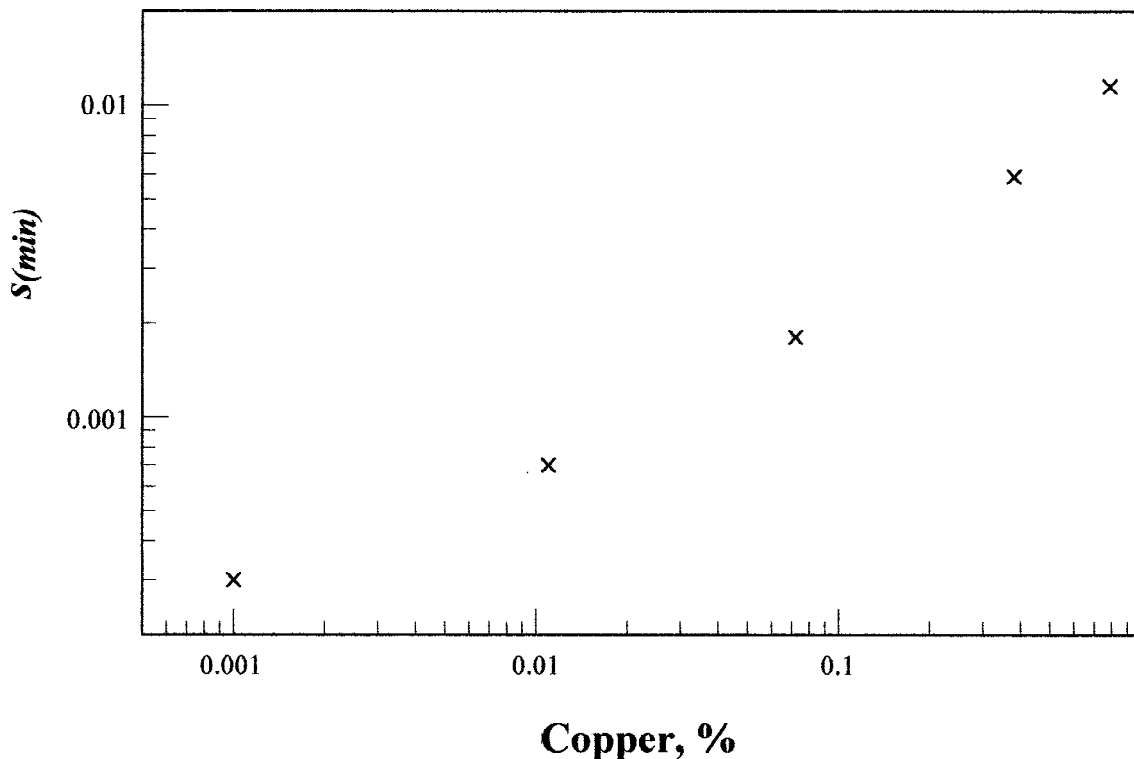


FIG. A1.1 Copper in Iron Ore by FAA

$$s_M = \sqrt{k_0^2 + (C \times k_{rel})^2} \quad (A1.5)$$

**A1.5 Case 2 Example**—Table A1.1 shows sensitivity statistics from an ILS employing 12 materials. The trends in  $s_M$  and  $s_{rel}$  are typical of data from methods that follow the general precision model for instrument sensitivity. The data was fit to Eq A1.5 using a standard non-linear technique. The sensitivity curve defined by the fitting constants  $k_0 = 0.0002$  and  $k_{rel} = 0.0094$  is shown on the plot of the data points in Fig. A1.2. The degrees of freedom for the sensitivity constants are 2 less than the sum of the individual values in the  $f$  column, 560 for this example.

**TABLE A1.1 Sensitivity Statistics for Copper in Iron and Steel by ICPS**

Material	Copper, % (C)	$s_M$	$s_{rel}$	$n$	$f$
1	0.00144	0.0001642	0.1138	23	46
2	0.00152	0.0001542	0.1011	23	46
3	0.00523	0.0002585	0.0494	23	46
4	0.01269	0.0001833	0.0144	24	48
5	0.01435	0.0002938	0.0205	19	38
6	0.02223	0.0003037	0.0137	24	48
7	0.02548	0.0003462	0.0136	25	50
8	0.04276	0.0006389	0.0149	25	50
9	0.06356	0.0008146	0.0128	20	40
10	0.1719	0.001844	0.0107	25	50
11	0.2166	0.002556	0.0118	25	50
12	0.2819	0.002104	0.0075	25	50

## A2. SPECIAL TESTS

**A2.1 Critical Parameters**—Simple instruments require no calibration for ordinary use. A marked meter scale or titration buret are examples. Most modern analytical instruments, on the other hand, measure complex physical properties. They require preliminary adjustments, calibrations, and periodic checks and readjustments to compensate for changing instrumental and environmental conditions if their inherent accuracy and precision are to be realized in normal use. The author of a method, through an understanding of the principles of operation of an instrument and its measurements, can identify a limited number of functions of primary importance in obtaining good results. A method user should be given the simplest possible tests to verify that the instrument exhibits adequate performance in those functions.

**A2.2 Instrument Types**—Methods may be classified by the physical properties measured. The following incomplete list includes examples of instruments and techniques important in the chemical analysis of metals, ores, and related materials:

**A2.2.1 Classical Analytical Techniques**—These techniques depend upon measurements of weight and volume. This practice does not address these methods because factors affecting their precision and accuracy are discussed in detail elsewhere.<sup>4</sup>

**A2.2.2 Molecular Absorption Spectrometry**—This technique depends upon measurements of light absorption by colored analyte species in solutions. Instrument response is strictly linear only over a restricted analyte concentration range. Methods typically specify calibration ranges in which response curves become non-linear for average instruments at higher analyte levels. Experience has shown that precision of measurements is unaffected by moderate curvature of the calibration curve, arbitrarily defined as a ratio of 0.70 or more between slopes at the high and low ends. With greater curvature, analysts in different laboratories produce hand-drawn curves that are dissimilar enough to affect between-laboratory precision. The same situation occurs for curves fit to

experimental data by different mathematical procedures: the greater the curvature, the larger the differences between results. Performance specifications of calorimeters or spectrophotometers require the linearity test outlined in A2.3.1.

**A2.2.3 Atomic Absorption Spectrometry**—This technique depends upon measurement of the absorption of a spectral line by an analyte in a sample solution sprayed into a high-temperature flame or evaporated into a heated carbon tube. The physical environment and processes for atomic absorption are different from molecular absorption, but the same arguments apply and lead to the same concerns about linearity of the calibration curves. Performance specifications of atomic absorption spectrometers require the linearity test (see A2.3.1).

**A2.2.4 Inductively-Coupled Plasma (ICP) or Direct-Current Plasma (DCP) Spectrometry**—These techniques depend upon measurements of the intensities of spectral lines of analytes emitted from a sample sprayed into a high temperature plasma produced by gases flowing through high-frequency alternating or direct-current electrical fields. This analytical technique is characterized by extensive usable calibration ranges. It is unnecessary to specify analyte levels so high that calibration curves do not meet the arbitrary linearity limit:  $\text{slope}_{\text{high}}/\text{slope}_0$  greater than 0.70. Methods written with this limitation in mind do not require linearity tests.

**A2.2.4.1** These instruments use programmed procedures provided by the instrument manufacturer for calibration based upon multielement calibration solutions. If prepared quantitatively from substances of known purity in accordance with a standard method, these solutions are superior to certified reference materials (see Practice E 2055). A critical requirement for spectrometers is to measure the intensity of an emission line of each analyte independent of radiation emitted by other sample components (including analytes). Methods shall provide procedures for identifying analyte wavelengths at which an interference of this kind occurs, and for correcting the instrument's response to eliminate the effect (usually with programmed procedures provided by the manufacturer). Plasma spectrometric methods require the spectral interference/background (I/B) tests outlined in A2.3.2.

### A2.3 Special Tests:

<sup>4</sup> Bassett, J., et al, *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th ed., 1978, Longman London and New York, pp. 59–82.

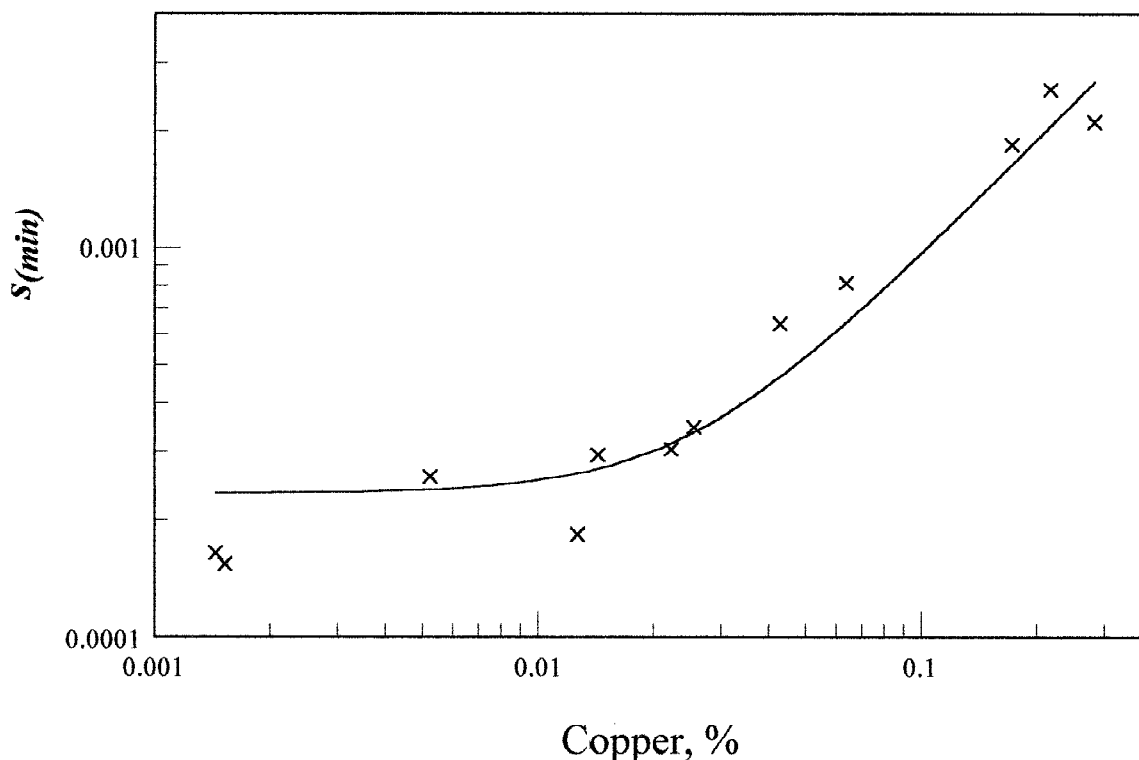


FIG. A1.2 Copper in Iron and Steel by ICP

**A2.3.1 Response Linearity Test**—The linearity test is a procedure to prevent users from attempting to calibrate an instrument at analyte levels too high for its capability. The test solutions are the calibration solutions prepared in the method, usually a “zero response” solution (corresponding to the origin of the calibration curve) and a series of 5 calibration solutions at equally-spaced analyte levels ending at the highest desired content. (If a method specifies a different number of equally-spaced calibration solutions, always perform the test with the lowest and highest pairs of readings.) If an instrument fails the test, the user repeats the test with equally-spaced solutions covering progressively lower analyte ranges until one is found for which the instrument passes the test. The method is then performed by calibrating the instrument over the final analyte range. Use the following text to describe the test: “*Instrument Response Linearity Test*—All readings for this test must be in instrument response units, not in concentrations. Obtain readings for the zero ( $x_0$ ) and the lowest ( $x_1$ ) and two highest ( $x_4$  and  $x_5$ ) of 5 equally-spaced calibration solutions. Calculate the linearity factor:  $lf = (x_5 - x_4) / (x_1 - x_0)$ . If  $lf$  is less than 0.7, the calibration range is too large. Prepare another set of 5 equally-spaced solutions covering a smaller range. Repeat until a range is found for which  $lf$  exceeds 0.7. The last set defines a range suitable for calibrating the instrument.”

**A2.3.2 Spectral Interference/Background (I/B) Test**—Plasma spectrometric instruments deliver samples and calibration materials to the instrument in solutions. Methods based upon these instruments provide users with relatively inexpensive analytical results traceable to well-defined reference materials. This performance is possible because by exercising only ordinary analytical skills, a user can prepare solutions having accurately known compositions for correcting and

calibrating instrument responses to yield accurate results for test materials. The instrumental processes for correction and calibration are outside the scope of this practice, however, they involve applying solutions specified in this test (or similar ones) in accordance with programmed procedures provided by instrument manufacturers for interelement and background correction and for multielement calibration. A user who has complied with the correction and calibration requirements of a method employs the I/B test to demonstrate that the instrument performs as expected.

**A2.3.2.1 I/B Tests**—Use the following text to provide detailed instructions for preparing test solutions and solutions needed to make the test solutions:

(1) Prepare a spike solution from the analyte standard solutions (used to prepare test solutions). Analytes are present in the spike solution at concentrations that yield concentrations near the low quantitative limits for each analyte when a measured volume is added to the test volume (for example, pipet 10 mL of spike solution into 100 mL volumetric flasks).

(2) Prepare one pure-base (PB) solution to yield results for analytes at or near zero concentration. This solution is made by treating a weight of pure base material equal to the test sample weight as test materials are treated, including the dissolution technique, addition of other reagents, if any, and dilution to volume (for example, for the analysis of 1-g titanium samples in 100 mL volume, weigh 1.00 g of titanium, dissolve in acids, and dilute to volume in a 100-mL volumetric flask).

(3) Prepare one spiked base (SB) solution to yield a relatively interference-free result for each analyte at a known low level. This solution is a pure-base solution to which a measured spike volume is added before dilution to volume.

(4) Prepare a set of I/B test solutions, BI-1 through BI- $n$ ,



**TABLE A2.1 Interference Matrix (IM) Table**

Analytical Wavelength		From SB (Low Levels)		From the BI- <i>n</i> Solution		BI-1	BI-2	BI-3	....
$\lambda_p$	Analyte	$\bar{x}_i$	$v_i$ Index	$\bar{x}_h$	$s_{rel\%}$	A, High	B, High	C, High	....
$\lambda_1$	A	$x_{A,1}$	$v_{A,1}$	$x_{A,h(1)}$	$s_{A,h(1)}$	column 5	$d_{B,1}$	$d_{C,1}$	....
$\lambda_2$	A	$x_{A,2}$	$v_{A,2}$	$x_{A,h(2)}$	$s_{A,h(2)}$	column 5	$d_{B,2}$	$d_{C,2}$	....
$\lambda_3$	B	$x_{B,3}$	$v_{B,3}$	$x_{B,h(3)}$	$s_{B,h(3)}$	$d_{A,3}$	column 5	$d_{C,3}$	....
$\lambda_4$	B	$x_{B,4}$	$v_{B,4}$	$x_{B,h(4)}$	$s_{B,h(4)}$	$d_{A,4}$	column 5	$d_{C,4}$	....
$\lambda_5$	B	$x_{B,5}$	$v_{B,5}$	$x_{B,h(5)}$	$s_{B,h(5)}$	$d_{A,5}$	column 5	$d_{C,5}$	....
$\lambda_6$	C	$x_{C,6}$	$v_{C,6}$	$x_{C,h(6)}$	$s_{C,h(6)}$	$d_{A,6}$	$d_{B,6}$	column 5	....
...	...	...	...	...	...	...	...	...	...

where  $n$  equals the number of elements to be tested. Each solution contains one element at its highest level with all other elements at their low spike concentration to demonstrate the extent of interference from the high element on the other analytes. The elements tested are usually the analytes, but non-reported elements should also be included if they vary among test materials at levels that may cause interference. In either case, interference occurs if an analyte's low-level result is increased or decreased by the presence of the high-level interfering element. B/I test solutions are prepared by adding the measured volume of interfering element standard solution to produce a concentration near its highest expected level, followed by the spike solution volume and a quantity of pure-base material calculated to make the sum of all added substances equal the sample weight (for example, if interfering and spike elements combined weigh 0.15 g, 0.85 g of titanium must be added for a sample weight of 1.00 g).

**A2.3.2.2 Spectral Interference/Background Method Development**—Record data obtained in the following steps:

(1) Use PB as the zero solution and BI-1 through BI- $n$  to perform approximate 2-point calibrations at one or more candidate analytical wavelengths for each element

(2) Set the instrument to report the mean and standard deviation of 4 readings at each wavelength for each test solution. Present solutions to the instrument in the order PB, SB, and BI (1 through  $n$ ). Obtain a second set of results for SB and compare with the first set. If instrument drift is evident, repeat all measurements to obtain consistent results.

(3) For each wavelength, combine the two sets of results obtained for SB – average means ( $\bar{x}_i$ ) and calculate root-mean-square (RMS) averages of standard deviations ( $s_0$ ). Prepare an interference matrix (IM) table with a row for each analytical wavelength and 6 more columns than the number of interfering elements (see Table A2.1). Label each row with the analytical wavelength and analyte it represents. Record  $\bar{x}_i$  for each row in the third column. Calculate  $v_i$  index = (4 times  $s_0$ ) for each row and record it in the next column. In each row, record the mean value of the element at its high level,  $\bar{x}_h$ , in the fifth column; calculate the relative percent standard deviation of  $\bar{x}_h$ ,  $s_{rel\%} = 100 (s_i/\bar{x}_h)$ , and record it in the next column. Head columns 7 through ( $n + 7$ ) with the interfering element/BI number. For BI-1 through BI- $n$ , record the result for the high-level analyte in the rows corresponding to its wavelengths. For the low-level analytes, calculate the difference at each wavelength between the observed result ( $x_\lambda$ ) and  $\bar{x}_i$  (from column 3), that is,  $d = (x_\lambda - \bar{x}_i)$ . Record the calculated  $d$ -value with proper sign in the appropriate row and column. If the absolute value of  $d$  is greater than the interference index,  $v_i$ , mark that wavelength for

further investigation to determine if the interference is caused by the low-level analyte as an impurity in the high element, radiation from the high analyte, or a change in background level.

**A2.3.2.3 Interpretation of I/B Experimental Data**—The I/B development test rapidly and systematically determines the extent of the development work required for plasma spectroscopic methods. In the initial survey, a developer includes the most promising analytical lines for analytes and other possibly interfering elements. The IM table provides useful comparisons, the  $v_i$  index for sensitivities at low analyte levels and  $s_{rel\%}$  for relative sensitivities at higher analyte concentrations. Smaller values indicate greater sensitivity. Possible interferences are signaled at wavelengths exhibiting large  $d$ -values. A scan of the nearby spectrum from the appropriate BI test solution reveals whether on-peak interelement correction or off-peak background correction is the appropriate procedure. Although all instruments do not exhibit exactly the same interference characteristics, the developer should include wavelength recommendations and the types of corrections required in the development laboratory as a guide to ILS participants and ultimate users of the method.

**A2.3.2.4 I/B Instrument Tests**—A slightly modified form of the I/B test is a convenient special instrument test for inclusion in the apparatus section of plasma spectroscopic methods. It is written into the method before the laboratory test phase of the ILS is started to enable the participating laboratories to provide I/B test data to be used in calculating acceptance criteria for inclusion in the method before it is balloted. Following manufacturer's recommended procedures, the method user sets up the instrument to perform the method using wavelength and interelement and background correction recommendations listed in the method. (A user unable to comply with the recommendations develops alternate wavelengths as already described.) Provide instructions for preparing  $m$  BI test solutions at the same time calibration solutions are prepared, each solution with one of the  $m$  analytes at the specified high level and all others at the specified low spike levels previously described. In preparation for running test samples the first time, use the full suite of calibration solutions to calibrate the instrument in accordance with the manufacturer's recommendations. Set the instrument to record results for the  $m$  analytes by averaging replicate readings in accordance with the method. In an ILS, laboratories report 3 sequential results for all analytes in each of the BI test solutions, interspersed with 3 sequential results on each test solution from ordinary ILS test materials. The ILS data for each analyte consists of ( $m - 1$ ) replicate sets at its known low spike level in the presence of a

high interfering element, one set at high analyte levels, and one set for each reference material selected for the study. The minimum standard deviations from the BI test solutions are used to calculate the performance criteria for instruments, while the reproducibility indexes are used in the precision and accuracy statement of the method. To use the method, a

laboratory runs the I/B test after calibrating the instrument, but before performing analyses the first time. If the difference between the results and the known values is less than the criteria provided in the apparatus section, the instrument demonstrates the capability of obtaining results conforming with the precision and accuracy statement of the method.

## APPENDICES

### (Nonmandatory Information)

#### X1. RATIONALE

X1.1 Although instruments have been used in methods of chemical analysis for hundreds of years, until relatively recently they have been treated as tools of physical measurement. In the scientific literature, they have been described in engineering fashion by dimensions, materials of construction, and physical function. Over the last quarter century, the concept of describing instruments by performance has evolved slowly in chemical analysis. The first method for chemical analysis of metals to explicitly incorporate this concept in specifying apparatus is Test Method E 396 (originally published in 1970), which specifies an atomic absorption spectrometric instrument in terms of defined performance tests. Few methods published since include specific tests and criteria, relying instead on references to Guide E 1024.

X1.2 A concept described by the term “performance-based methods” has enjoyed recent popularity, supported by an exaggeration: “even though not performed in accordance with its text, a performance-based method yields valid results if performance criteria for the final measurements are met.” The scientific basis for validity of results from standard methods is that they are reproducible in different laboratories. Reproducibility indexes established in an ILS are valid only if laboratories follow the method tested in the study. Claims are made that laboratories can make major changes in standard methods and still be assured by a simple test (for example, recovery of

an added spike) that results conform to the stated accuracy and precision. These claims must be viewed with suspicion. They confuse a one-time test of the instrument at the analyte level of the performance test with an interlaboratory test of the entire method. Even methods instructing the user to perform the experimental work necessary to fully develop a method cannot rightfully lead the user to expect results with the precision and accuracy derived from an ILS unless the user develops essentially the method tested in the ILS. If the new method differs significantly from the tested standard method, its performance may be quite different from that of the standard method. Furthermore, the new method’s performance cannot be determined in a single laboratory. It must be established by a valid statistical study of its performance in many laboratories.

X1.3 This practice was undertaken for two reasons. First, to disabuse task groups and method users of the idea that methods can be written in vague, general terms permitting users wide latitude in implementing them, and still preserve statistical performance equal to that of similar, but strictly written, methods. Second, to promote among task groups and method users the idea that instruments can be specified in general terms that permit users to employ a standard method on their own equipment if it meets experimentally determined criteria in accordance with designed tests.

#### X2. F-STATISTIC AND CRITICAL VALUES FOR THE INSTRUMENT SENSITIVITY TEST

X2.1 *F-Statistic*—Variability observed in the user’s laboratory,  $s_U$ , if compared with the pooled variability,  $s_M$ , from the ILS provides a warning that a user’s instrument exhibits more variability than the average ILS instrument. The statistic required is:

$$F_{(f_1, f_2)} = \frac{s_U^2}{s_M^2} \quad (\text{X2.1})$$

The critical value of  $F$  depends upon the degrees of freedom ( $f$ ) of both  $s_U^2$  and  $s_M^2$ . The variance,  $s_U^2$ , is calculated from 10 readings, and its degrees of freedom,  $f_1$ , always equal 9. However, the degrees of freedom for  $s_M^2$ ,  $f_2$ , depend upon the number of participating laboratories,  $p$ , and the number of

replications,  $n$ , reported by each laboratory at a specified analyte level,  $A$ :

$$(f_2)_A = p_A (n - 1) \quad (\text{X2.2})$$

X2.2 *Sensitivity Test*—If the ratio of the user’s variances to the ILS variance (both measured at analyte level  $A$ ) does not exceed the critical value for the  $F$  distribution, the test concludes that, at the confidence level chosen for  $F$ , the instrument’s variability is no greater than the minimum variability demonstrated in the method’s ILS. That condition is indicated by the following inequality:

$$(F_{(9, f_2)})_A > \frac{s_U^2}{s_M^2} \quad (\text{X2.3})$$

If the task group rearranges the inequality and calculates the right-hand expression at the analyte level or levels which most challenge the instrument, the test becomes:

$$(s_U^2)_A < (F_{(9,f_2)} \times s_M^2)_A \quad (\text{X2.4})$$

E 1601, an ILS requires 6 or more independent sets of data and 3 or more replicate results. Table X2.1 provides the critical *F*-values a task group needs to calculate criteria for satisfactory instrument performance.

### X2.3 Critical values for *F*—In accordance with Practice

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