Designation: E 2054 – 99

Practice for Performance–Based Description of Instruments in Chemical Analysis Methods[1]

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 (ε) 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:* [2]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 396 Test Method for Chemical Analysis of Cadmium

E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E 1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

E 1914 Practice for the Use of Terms Relating to the Development and Evaluation of Methods of Chemical Analysis

E 2055 Practice for Referencing Methods for Chemical Analysis of Metals and Related Materials

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.

[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.

Current edition approved Dec. 10, 1999. Published February 2000.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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:

$$s_{rel} = s_H/\bar{x}_H \tag{1}$$

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:

$$s_{rel} = s_M/\bar{x} \tag{2}$$

Calculate the degrees of freedom:

$$f = p \times (n - 1) \tag{3}$$

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:

$$I_0 = \sqrt{k_0^2 \times F_0} \tag{4}$$

$$I_{rel} = \sqrt{k_{rel}^2 \times F_{rel}} \tag{5}$$

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}:

$$s_{rel} = s_H/\bar{x}_H \tag{6}$$

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 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

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:

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

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

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:

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

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

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, $C_1 ... C_m$, 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:

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

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.

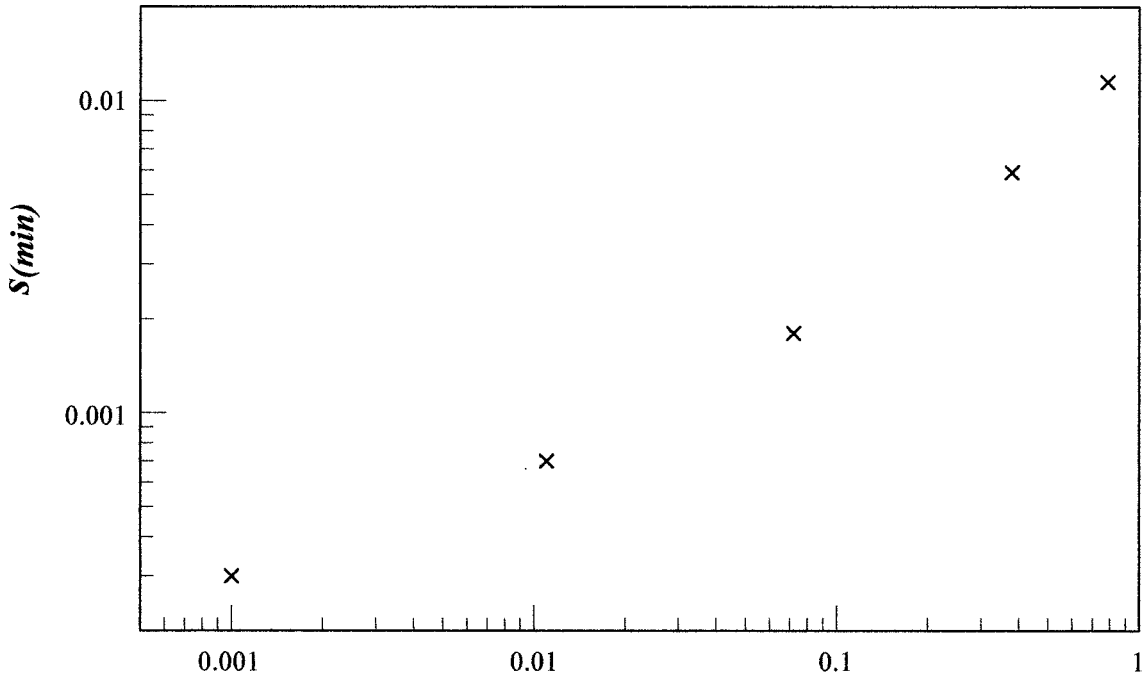

FIG. A1.1 Copper in Iron Ore by FAA

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