Standard Practice for
Evaluating an Optical Emission Vacuum Spectrometer to Analyze Carbon and Low-Alloy Steel[1]

This standard is issued under the fixed designation E 1009; 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 evaluation of an optical emission vacuum spectrometer to analyze carbon and low-alloy steels. It covers instruments used for the analysis of solid samples taken from molten metal for production control or from products to confirm the composition. Both pre-installation and post-installation precision and accuracy are included in the evaluation.

1.2 While Tables 1-3 are specific for plain carbon and low-alloy steel, they could be supplemented by similar tables for other materials.

1.3 *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[2]
E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves[2]
E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis[2]
E 528 Practices for Grounding Basic Optical Emission Spectrochemical Equipment[3]
E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data[2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology E 135 and Practice E 876.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *accuracy*—the closeness of a spectrochemical determination to an accepted reference; it is affected by imprecision and bias.

3.2.2 *standard error (SE)*—although primarily a calculation that measures how well a calibration has been defined, standard error (SE) is used in this practice as an indicator of accuracy. It is CRM-dependent and instrument-operator dependent. Some expected maximum SE values are listed, but comparisons between instrument calibrations can strictly be done only when identical suites of calibrants are used.

4. Summary of Practice

4.1 After the spectrometer is calibrated, use this practice to evaluate the instrument and its calibration. Certified reference materials are run as unknowns and precision is compared to Table 1. Before comparing standard errors to those in Table 2, ascertain that the calibration does not include unrealistic inflections. Values equal to or less than those in Tables 1 and 2 indicate that the instrument is acceptable.

5. Significance and Use

5.1 Periodically throughout the useful life of an optical emission spectrometer it becomes necessary to evaluate its performance. This is especially true at manufacture and during installation. The objective at this time is to establish whether the instrument meets design specifications and performs to customer specifications. A manufacturer's objective may be to compare production line instruments. With data on many instruments, such an evaluation procedure would be a valuable contribution to the manufacturer's quality control plan.

5.2 Use of this procedure at installation can tell the manufacturer or user whether there has been a significant change in performance due to faulty shipping or handling of the instrument. At this time, the procedure could be the beginning of a quality control plan for the user. Once established, the data from the procedure provide a base for comparison of future runs, enabling operators to detect changes in performance.

5.3 Data produced by this practice make possible a comparison of different instruments, for example, X-ray and optical emission or optical emission and atomic absorption. While the data in the Tables 1-3 are valid for optical emission spectrometers, other instruments may produce better or worse performance values. In this manner, the data could be used by management to determine the suitability of a given instrument

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[1] This practice is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores and Related Materials and is the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.
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[2] *Annual Book of ASTM Standards*, Vol 03.05.
[3] Discontinued 1999; see *1998 Annual Book of ASTM Standards*, Vol 03.06.

to perform a given determination with an acceptable precision and accuracy.

TABLE 1 Recommended Precision Requirements For Steel Using An Optical Emission Vacuum Spectrometer[A]

Element	Approximate Concentration, %	Standard Deviation
C	0.06	±0.002
	0.15	0.004
	0.50	0.010
	0.90	0.015
Mn	0.35	0.007
	0.60	0.015
	1.00	0.02
	1.50	0.03
P	0.006	0.0007
	0.04	0.0015
S	0.005	0.0015
	0.04	0.002
	0.06	0.004
Si	0.02	0.004
	0.30	0.006
	0.50	0.010
Ni	0.03	0.002
	0.10	0.003
	0.70	0.007
	1.60	0.03
Cr	0.04	0.002
	0.30	0.007
	0.80	0.015
Sn	0.003	0.0006
	0.02	0.0015
	0.05	0.002
V	0.01	0.0015
	0.03	0.002
	0.25	0.007
Mo	0.03	0.003
	0.30	0.008
Cu	0.02	0.0007
	0.15	0.003
Ti	0.02	0.002
	0.20	0.008
Al	0.006	0.002
	0.02	0.003
	0.07	0.004
Nb	0.02	0.0015
	0.07	0.003
B	0.001	0.00015
	0.07	0.003
Zr	0.05	0.002
Pb	0.01	0.0015
Se	0.02	0.002

[A] These precisions were generated from actual data in one laboratory; as such, they represent what *has* been done with proven, homogeneous materials.

TABLE 1 (*a*) Revised Data

Element	Approximate Concentration, %	Standard Deviation
C	0.015	0.0009
C	1.03	0.012
MN	0.067	0.0006
Mn	2.00	0.023
P	0.0032	0.0007
S	0.0024	0.0001
Si	0.01	0.0002
Ni	0.021	0.0004
Ni	2.00	0.005
CR	1.48	0.009
Mo	0.005	0.0004
Mo	0.50	0.002
Cu	0.015	0.0003
Cu	0.30	0.0007
Ti	0.0055	0.0004
Al	0.004	0.0004
Al	0.04	0.0007
Nb	0.01	0.0005
Nb	0.1	0.002
B	0.001	0.0001
B	0.005	0.0001
Zr	0.013	0.0007
Pb	0.002	0.0004
As	0.01	0.0003
As	0.055	0.002

[A] These precisions were generated from data that were collected on newer instruments than the original data.

TABLE 2 Elements, Concentration Ranges, and Recommended Acceptable Standard Error (SE) for Steel

Element	Approximate Concentration Range, %, as Covered by the Certified Standards	Max Allowable Standard Error, %[A]
C	0.02 to 1.00	0.009
Mn	0.01 to 1.50	0.012
P	0.001 to 0.07	0.002
S	0.003 to 0.06	0.002
Si	0.005 to 1.00	0.012
Ni	0.01 to 2.00	0.014
Cr	0.01 to 1.00	0.012
Sn	0.002 to 0.10	0.002
V	0.002 to 0.50	0.005
Mo	0.003 to 0.50	0.005
Cu	0.005 to 0.50	0.007
Ti	0.003 to 0.25	0.005
Al	0.005 to 0.25	0.005
Nb	0.002 to 0.30	[B]
B	0.0001 to 0.04	0.001
Zr	0.01 to 1.00	[B]
Pb	0.001 to 0.03	[B]
Se	0.001 to 0.05	[B]

[A] These values will depend on the standards used and the distribution of their compositions throughout the range of calibration.
[B] Accuracy will not be assessed for these elements due to lack of CRM's.

5.4 While this practice is directed towards optical emission vacuum spectrometers in the analysis of carbon and low-alloy steel, its use is not restricted to that instrument or that matrix.

6. Instrumentation

6.1 The vacuum spectrometer shall be equipped with an argon-flushed sample stand for point-to-plane excitation.

6.2 The excitation parameters and radiations measured shall be selected to meet the specified performance.

TABLE 3 Sample Calculation of Standard Error (SE)[A]

Given, %	Calculated, %	Difference (d), %	d^2
0.19	0.189	0.001	0.000001
0.27	0.274	−0.004	0.000016
0.42	0.432	−0.012	0.000144
0.51	0.526	−0.016	0.000256
0.99	0.987	0.003	0.000009
1.29	1.289	0.001	0.000001
2.33	2.338	−0.008	0.000064
2.97	2.961	0.009	0.000081

[A] The sample SE calculation follows:

$$\Sigma d^2 = 0.000572$$

$$\Sigma d^2/n = 0.0000715$$

$$SE = \sqrt{\Sigma d^2/n} = 0.008$$

where:
n = 8

NOTE 1—Ordinarily this selection is made by the vendor, or instrument manufacturer, based on experience.

6.3 Provision shall be made to compensate for spectral interferences. More than one spectral line may be provided for an element, depending on element concentration or the excitation used, but switching of lines shall be done automatically.

7. Analysis Time

7.1 Analysis time, excluding sample preparation, shall not exceed 30 s for single burns, or 60 s for multiple burns.

NOTE 2—This requirement may be waived if speed of analysis is not required. The time limitation does not apply to resulfurized grades of steel and may be changed for other special grades of steel.

8. User's Responsibility for Laboratory Environment

8.1 Maintain laboratory temperature and humidity as required by the spectrometer. The generally accepted ranges are 18.5 to 24°C (65 to 75°F) and 20 to 50 % relative humidity.

8.2 Provide argon that meets the requirements for vacuum spectrometers and is in accordance with Practice E 406. In some cases argon purity of 1 ppm is required.

8.3 Provide the required electrical power regulated to ± 5 % and filtered to prevent radio frequency interference. See Practice E 528.

8.4 Provide a radio-frequency ground in accordance with Practice E 528. Modern excitation sources may not require special grounding.

9. Purpose of Analytical Performance Tests

9.1 *Pre-Shipment Precision*:

9.1.1 Perform the tests in 10.1 to verify performance before shipment so that any necessary adjustments can be made at the factory. Preliminary calibration of the spectrometer is required to assure that the concentration range specified for each element is covered and to provide analytical curves for reporting analytical precision in terms of percent concentration.

NOTE 3—Raw data output is adequate if the slope of the curve is defined.

9.2 *Post-Installation Precision*:

9.2.1 Repeat the tests in 10.1 to confirm previous calibrations. The post-installation test shall be made by the customer after training operators and verifying that the calibrations are satisfactory. The vendor may send a representative to consult on and witness this test.

9.3 *Pre-Shipment Accuracy*:

9.3.1 Perform the tests in 10.2. This provides a measure of accuracy based on how closely the spectrometer response agrees with the certified values of the CRMs when needed interference corrections are made.

9.3.2 When evaluating spectrometers equipped with dedicated computers or calculators, this test also demonstrates the ability of the software to (*1*) For curves that cover a wide concentration, an improvement in accuracy may be achieved by defining the upper and lower concentrations separately, with a smooth transition from one segment to the other, (*2*) Define interelement effects, (*3*) Establish correction factors, and (*4*) Convert raw data output into percent concentration.

9.4 *Post-Installation Accuracy*:

9.4.1 Repeat the tests of 10.2 using the identical reference materials used in 9.3.1.

9.4.2 This test shall be done with trained operators and the vendor may send a representative to consult on and witness this test.

10. Test Procedures

10.1 *Precision*:

10.1.1 The purchaser shall provide four to six reference materials of proven homogeneity covering the approximate concentrations listed in Table 1.

10.1.2 Analyze the set of test specimens randomly at least ten times during two separate 4-h periods. Each is to be a single burn. Warm-up runs are permitted at the start of each test period. Adjustment of optical alignment and standardization shall be made at the start of each period. Standardization shall not be done more than once every 2 h thereafter.

10.1.3 Compute the standard deviation, *s*, for each element in each material of 10.1.1 based on the combined analyses from each test period as follows:

$$s = \sqrt{\Sigma d^2/(n-1)} \qquad (1)$$

where:
d = deviation of each determination from the mean, and
n = number of determinations.

10.1.4 The test results are satisfactory if the precision or imprecision, in terms of standard deviation, is equal to or less than that listed in Table 1.

10.2 *Accuracy*:

10.2.1 Select the CRMs for calibration from those listed in Note 5. See also Note 6.

10.2.2 These same CRMs shall be used to calculate the standard error as defined in 10.2.6.

NOTE 4—If this evaluation is to include an element not certified, then the reference materials used must be from an accepted and reliable source.

10.2.3 If this procedure is to be considered an arbitration test, the calibration reference materials must be acceptable to both parties, and both parties must have access to them.

10.2.4 After the spectrometer is calibrated, analyze the same reference materials one time each.

10.2.5 If adjustments to the spectrometer are required during this test, discard the results and repeat the test. If the evaluation of an element does not satisfy the accuracy requirements, the test may be repeated and the results substituted for the first results.

10.2.6 Compute the standard error, *SE*, as follows:

$$SE = \sqrt{\Sigma dc^2/f} \qquad (2)$$

where:
dc = difference between the certified and the calculated values, and
f = the degrees of freedom in the observations.

The value to use for f is discussed in Practice E 876. If the CRMs are calculated as if they were unknowns in an established calibration, as directed in 10.2.4, f will be the number of reference materials. If an alternate procedure is used in which the CRMs are calculated from a calibration equation that they define from a regression as given in Practice E 305, f is reduced by the order of the equation, the number of constants it contains.

10.2.7 Sample calculation of SE is given in Table 3.

10.2.8 The results of the test are satisfactory if the SE is equal to or lower than that listed in Table 2.

Note 5—These certified reference materials have proven to be satisfactory for calibration and calculation of SE as specified in this practice: NIST (NBS) SRM 1761 to 1767, 1261, 1263 and 1264. Other certified reference materials of similar compositions available from BAS, ISIJ, and IRSID may also be used.

Note 6—Table 2 assumes that most of the concentrations will be in a range considered to be in the "straight-line portion" of the analytical curve. Not all curves have such; some have only that, depending on the element and the range to be covered by an instrument. Some do not have background while some have only that area to contend with. If it is possible to do so, use a balance of reference materials in each region of background, straight-line, and reversal for the test. Weighting of reference materials in a given extreme area, will affect the SE achieved. Table 2 is recommended, based on the experience of one laboratory. Values can be substituted but should be agreed upon beforehand.

11. Keywords

11.1 carbon steel; low-alloy steel; optical emission; vacuum spectrometer