



Standard Practice for Optimization of Electrothermal Atomic Absorption Spectrometric Equipment¹

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1. Scope

1.1 This practice covers the optimization of electrothermal atomic absorption spectrometers and the checking of spectrometer performance criteria.

1.2 The values stated in SI units are to be regarded as the standard.

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:*²

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data³

E 1184 Practice for Electrothermal (Graphite Furnace) Atomic Absorption Analysis

E 1452 Practice for Preparation of Calibration Solutions for Spectrophotometric and for Spectroscopic Atomic Analysis³

3. Significance and Use

3.1 This practice is for optimizing the parameters used in the determination of trace elements in metals and alloys by the electrothermal atomic absorption spectrometric method. It also describes the practice for checking the spectrometer performance. The work is expected to be performed in a properly

equipped laboratory by trained operators and appropriate disposal procedures are to be followed.

4. Apparatus

4.1 *Atomic Absorption Spectrometer with Electrothermal Atomizer*, equipped with an appropriate background corrector, a signal output device such as a video display screen (VDS), a digital computer, a printer or strip chart recorder, and an autosampler.

4.2 *Grooved Pyrolytic Graphite-Coated Graphite Tubes*, conforming to the instrument manufacturer's specifications.

4.3 *Pyrolytic Graphite Platforms*, L'vov design, fitted to the tubes specified in 4.2.

4.4 *Pyrolytic Graphite-Coated Graphite Tubes*, platformless, conforming to the instrument manufacturer's specifications.

4.5 *Radiation Source for the Analyte*—A hollow cathode lamp or electrodeless discharge lamp is suitable.

NOTE 1—The use of multi-element lamps is not generally recommended, since they may be subject to spectral line overlaps.

4.6 For general discussion of the theory and instrumental requirements of electrothermal atomic absorption spectrometric analysis, see Practice **E 1184**.

5. Reagents

5.1 *Purity and Concentration of Reagents*—The purity and concentration of common chemical reagents shall conform to Practices **E 50**. The reagents should be free of or contain minimal amounts (<0.01 µg/g) of the analyte of interest.

5.2 *Magnesium Nitrate Solution* [2 g/L $Mg(NO_3)_2$]—Dissolve 0.36 ± 0.01 g high-purity $Mg(NO_3)_2 \cdot 6H_2O$ in about 50 mL of water, in a 100-mL beaker, and transfer the solution into a 100-mL volumetric flask. Dilute to mark with water and mix. Store in polypropylene or high-density polyethylene bottle.

5.3 *Calibration Solutions*—Refer to the preparation of calibration solutions in the relevant analytical method for the determination of trace elements in the specific matrix. Calibration solution S_0 represents the calibration solution containing no analyte; S_1 the least concentrated calibration solution; S_2 the calibration solution with the next highest concentration;

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 E01.20 Fundamental Practices.

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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.

³ Withdrawn.

through S_k , the most concentrated calibration solution. Also refer to Practice E 1452.

5.4 *Matrix Modifiers*—Refer to the relevant analytical method for the determination of trace elements in the specific matrix.

6. Initial Checks and Adjustments

6.1 Turn on power, cooling water, gas supplies, and fume exhaust system.

6.2 Open the furnace to inspect the tube and contacts. Replace graphite components, if wear or contamination is evident. Inspect windows and clean or replace as required.

6.2.1 New graphite contacts or new tubes should be conditioned prior to use, in accordance with the heating program recommended by the manufacturer.

6.2.1.1 In the absence of manufacturer's recommendations, a conditioning program for a graphite furnace is shown in Table 1.

7. Radiation Source

7.1 Install and operate hollow cathode lamps or electrodeless discharge lamps in accordance with the manufacturer's instructions.

7.2 After the manufacturer's prescribed warm-up time, the signal from the radiation source should not deviate by more than 0.5 % from the maximum value (that is, by not more than 0.002 absorbance units) over a period of 15 min. Significantly greater fluctuations are usually indicative of a faulty lamp or power supply.

8. Spectrometer Parameters

8.1 *Wavelength*, as specified by the appropriate procedure.

8.2 *Slit Width*, as recommended by the manufacturer. Where two slit height settings are available, select the shorter height.

8.3 *Background Correction*:

8.3.1 *Zeeman Background Correction System*:

8.3.1.1 Ensure that the poles of the magnet are clean and securely tightened.

8.3.1.2 If necessary, set the optical temperature sensor in accordance with the instrument manufacturer's instructions.

8.3.2 *Continuum Background System*:

8.3.2.1 Select the background correction option and allow lamps to stabilize for 30 min. Verify that the energies of the analyte lamp and the deuterium lamp are balanced within tolerances recommended by the manufacturer.

8.3.2.2 If necessary, set the optical temperature sensor in accordance with the instrument manufacturer's recommendation.

8.3.3 To check the performance of the background correction system, measure the atomic background absorbance of 20 μ L of 2 g/L magnesium nitrate solution at a wavelength in the 200 to 250 nm region (for example, Bi 223.1 nm) using a dry temperature of 120°C, a pyrolysis temperature of 950°C, and an atomization temperature of 1800°C. A large background signal should be observed with no over-or under-correction of the atomic signal.

NOTE 2—In general, Zeeman systems should compensate for background levels as high as 1.0 to 1.5 absorbance units. A continuum correction system should be able to correct for the broad-band background absorbance up to 0.5 to 0.6 absorbance units.

8.4 *Autosampler*—Check operation of the autosampler. Pay particular attention to the condition of the pipette tip and position of the tip during sample deposition. Clean the pipette tip with methanol. Adjust in accordance with the manufacturer's instructions.

NOTE 3—Use of an appropriate surfactant in the rinse water may enhance operation. If a surfactant is used, it should be checked for the presence of all the analytes to be determined.

9. Optimization of the Furnace Heating Program

9.1 Optimization of the furnace heating program is essential. Furnace programs recommended by the manufacturers are often designed for samples of a completely unrelated matrix. The analyst shall optimize the furnace program for a particular sample matrix (for example, steel, nickel alloys, etc.) and modifier system in accordance with the following procedure:

Furnace Step	Section
Drying	9.2
Pyrolysis	9.3
Atomization	9.4
Clean-out	9.5

9.2 Drying Step:

9.2.1 Select the graphite tube type (L'vov or platformless) and measurement mode (peak height or integrated peak area). Then select the same heating parameters used in 8.3.3. Optimize the drying parameters using any of the calibration solutions (see 5.3) and the procedure given in either 9.2.2 or 9.2.3.

9.2.2 *Samples Deposited on the Tube Wall*—For wall-deposited samples, a drying temperature of 120°C is satisfactory. To avoid spattering, a 20 s ramping time should be used to reach the 120°C temperature and then held at that temperature. The holding time will depend on the volume of the sample introduced. Typical holding times are as follows:

Injected Volume, μ L	Holding Time, s
10	15
40	30

9.2.3 Samples Deposited on the L'vov Platform:

9.2.3.1 When using a L'vov platform, a two-stage drying process is beneficial to prevent spattering.

9.2.3.2 In the first stage, heat the sample rapidly to 80°C, using a 1 s ramp and then hold the temperature at 80°C for a short time. The holding time depends upon the volume of the solution injected. Typical holding times are shown in 9.2.2.

TABLE 1 Program for Graphite Furnace Conditioning

Step	Temperature, °C	Ramp, s	Hold, s	Gas flow, mL/min
1	1500	60	20	300
2	20	1	10	300
3	2000	60	20	300
4	20	1	10	300
5	2600	60	10	300
6	20	1	10	300
7	2650	2	5	0

9.2.3.3 For the second stage, the temperature is ramped over a period of 20 to 30 s, to a value 20 to 40°C above the boiling point of the solvent. The holding times should be the same as given in 9.2.3.2.

9.2.4 In both cases, select a preliminary set of drying conditions and monitor the drying process visually with the aid of a dental mirror, to ensure that it proceeds without spattering. Hold the mirror directly above the sample introduction port (avoid touching the magnet), or near the end windows of the graphite tube. Observe vapor formation on the mirror as drying proceeds. Vapor evolution should cease at approximately 10 s before the end of the drying step. Adjust the hold times accordingly to accomplish this.

9.2.4.1 **Warning:** To prevent serious eye injury, do not view the tube directly during the atomization or clean-out steps.

9.3 Pyrolysis Step:

9.3.1 During this step, volatile components of the matrix are driven off and precursory reactions occur (for example, reduction of the analyte oxide to the elemental state and the formation of matrix refractory oxides and carbides).

NOTE 4—Because of the low volatility of most metal alloy matrices, most of the matrix will remain in the furnace after the pyrolysis.

9.3.2 Use the optimum drying conditions as determined in 9.2.

NOTE 5—At this stage, both the optimum pyrolysis and atomization temperatures are unknown. An estimate of the suitable atomization temperature shall be made and entered into the instrument prior to optimization of the pyrolysis temperature.

9.3.3 Set atomizing temperature according to the manufacturer's instructions. Select the "Gas Interrupt" (or "Gas Stop") option. Select an atomization integration time of 10 s.

9.3.4 Select a pyrolysis time of 30 s ramp and 30 s hold.

9.3.5 Select a calibration solution (see 5.3) which will give an absorbance reading of 0.2 to 0.4 absorbance units.

9.3.6 Vary the pyrolysis temperature in increments of 100°C, throughout the range from 500 to 1400°C, taking three absorbance measurements at each step for the calibration solution selected in accordance with 9.3.5.

9.3.7 Calculate the mean of the three absorbance measurements obtained for each temperature step. Plot a graph relating the pyrolysis temperature to the mean absorbance. Note the temperature at which the absorbance starts to decline. Subtract 50°C from this value to obtain the optimum pyrolysis temperature.

NOTE 6—The 50°C allowance accommodates the day-to-day variations in the working temperature of the system.

9.3.8 Use the optimum pyrolysis temperature found, and vary the hold time over the range of 15 to 60 s (15 s intervals). Take three absorbance measurements at each step for the calibration solution selected in accordance with 9.3.5. Monitor the background signal during the process, and note the time at which the background signal returns to the baseline.

9.3.9 Calculate the mean of the three absorbance measurements. There should be no evidence of analyte loss (indicated by lower absorbances for the longer hold times).

9.3.10 Provided the pyrolysis condition in 9.3.7 is satisfied, select the shortest time in which the background signal returns to the baseline and add 10 s to this value to obtain the optimum hold time.

NOTE 7—A slow ramp time of 30 s and a hold time of 30 s is usually sufficient for all pretreatment reactions to occur. Short ramp times may provoke explosive loss of sample in the tube.

9.4 Atomization Step:

9.4.1 This step involves the production of gaseous analyte atoms inside the graphite tube.

9.4.2 The analyst should determine the optimum atomization temperature and integration time experimentally, using the same "Gas Interrupt option," graphite tube type, and measuring mode combination selected before the optimization of the drying step.

NOTE 8—Although it is possible to optimize the L'vov platform using the peak height measurement mode, the atomization step shall be optimized in such a manner that the conditions required for stabilized temperature platform furnace (STPF) operation are satisfied. In addition to the use of "Gas Interrupt" and matrix modification (inherent in certain procedures), the following additional conditions are to be satisfied: (1) The temperature difference between the pyrolysis step and the atomization step should be as small as possible (less than 1000°C). This allows the furnace to approach the near isothermal conditions quickly and reduces the amount of matrix volatilized; (2) Peak area integration measurement mode shall be used; and (3) There shall be zero ramping time between the pyrolysis and the atomization steps. The "Gas Interrupt" will interrupt the flow of inert gas through the graphite tube from a few seconds prior to the start of the atomization cycle to the end of the atomization cycle.

9.4.3 Use the optimum drying and pyrolysis conditions.

9.4.4 Select an atomization temperature of 1200°C and an integration time of 20 s.

9.4.5 Obtain three absorbance measurements with the calibration solution used in 9.3.5.

9.4.6 Repeat varying the atomization temperature in 100°C increments up to 2500°C. It is not necessary to continue raising the atomization temperature once the absorbance reaches a plateau.

9.4.7 Plot the mean of the three absorbance measurements obtained for each step against the atomization temperature.

9.4.8 Examine the graph and determine the lowest atomization temperature where maximum absorbance was obtained. Add 200°C to this value to obtain the optimum atomization temperature.

NOTE 9—At the lowest atomization temperature that gives maximum absorbance when using the peak area integration mode, the peaks may be broad with considerable trailing. The extra 200°C will overcome this problem.

NOTE 10—If the L'vov platform is used in the STPF conditions, the difference between the optimum pyrolysis temperature and optimized atomizing temperature does not exceed 1000°C.

9.4.9 Using the optimum atomization temperature, start with a holding time of 10 s. Proceed to 9.4.9.1 for instruments equipped with a VDS or fast recorder. Follow the procedure given in 9.4.9.2 for instruments without this equipment.

9.4.9.1 For instruments equipped with VDS or fast recorder, measure the calibration solution and observe the atomic signal during the atomization stage. Determine the optimum hold

time by adding 1 s to the time taken for the trace to return to the zero axis of the absorbance scale.

9.4.9.2 For instruments without a VDS or a fast recorder, make three absorbance measurements of the calibration solution. Calculate the mean absorbance. Repeat the measurements using progressively shorter hold times (1-s intervals) until the mean of the three measurements starts to decrease. Add 1 s to the hold time at this point to obtain the optimum hold time.

9.5 *Clean-Out Step*—Heat the furnace at 2650°C for 5 s to remove the residual matrix.

NOTE 11—In practice, the matrix elements cannot be completely removed, even at high temperatures.

10. Instrument Performance Criteria

10.1 After the furnace heating program has been optimized, the following tests shall be performed, using the criteria and the calibration solutions (see 5.3) specified in the analytical method being used.

10.2 *Characteristic Mass*, m_c —The amount of analyte required for 1 % absorption (0.0044 absorbance units) is dependent upon the element and the instrument used, and is calculated as follows:

10.2.1 Measure the absorbance of calibration solution S_0 three times. Calculate the mean absorbance A_0 .

10.2.2 Measure the absorbance of calibration solution S_1 three times. Calculate the mean absorbance A_1 .

10.2.3 The characteristic mass, m_c , is given by the following equation:

$$m_c = 0.0044CV/(A_1 - A_0) \quad (1)$$

where:

C = concentration of the analyte in calibration solution S_1 , ng/mL, and

V = volume of calibration solution S_1 injected, μL .

10.3 Measurement Variability:

10.3.1 See Practice E 876 for definitions of terms and explanation of calculations.

10.3.2 Measure the absorbance of the least concentrated calibration solution, S_1 , ten times using the injection volume recommended in the relevant analytical method. Record the individual readings A_1 and calculate the mean value, A_1 .

10.3.2.1 Calculate the standard deviation, s , for the least concentrated calibration solution, S_1 , using the following equation:

$$S_A = \sqrt{[\sum(A_1 - A_1)^2]/9} \quad (2)$$

10.3.2.2 Calculate the relative standard deviation, RSD , for the absorbance measurement of calibration solution S_1 , using the following equation:

$$RSD_{S_1}, \% = 100 S_A/A_1 \quad (3)$$

10.3.3 Measure the absorbance of the most concentrated calibration solution, S_K , ten times using the injection volume

recommended in the relevant analytical method. Record the individual absorbance readings, A_k and calculate the mean value, A_k .

10.3.3.1 Calculate the standard deviation, s for the most concentrated calibration solution, S_K , using the following equation:

$$S_B = \sqrt{[\sum(A_k - A_k)^2]/9} \quad (4)$$

10.3.3.2 Calculate the relative standard deviation, RSD , for the absorbance measurement for the most concentrated calibration solution, S_K , using the following equation:

$$RSD_{S_K}, \% = 100 s_B/A_k \quad (5)$$

10.4 Detection Limit, $m_{\min}$:

10.4.1 Measure the absorbance of calibration solution S_0 ten times, using the injection volume recommended in the relevant analytical method. Record the individual absorbance readings, A_0 and calculate the mean value A_0 .

10.4.2 Measure the absorbance of calibration solution S_1 ten times, using the injection volume recommended in the relevant analytical procedure. Record the individual absorbance readings, A_1 and calculate the mean value A_1 .

10.4.3 Obtain the standard deviation of the least concentrated calibration solution S_1 as described in 10.3.2 and 10.3.2.1.

10.4.4 Calculate the limit of detection, $m_{\min}$ picograms, using the following equation:

$$m_{\min} = 2 CV_{S_A}/(A_1 - A_0) \quad (6)$$

where:

C = concentration of the analyte in calibration solution S_1 , ng/mL,

V = volume of the solution injected, μL , and

S_A = standard deviation of calibration solution S_1 .

10.5 Graph Linearity, L :

10.5.1 Measure the set of calibration solutions in triplicate. Calculate the mean of the three absorbances obtained for each solution.

10.5.2 Plot a graph relating the mean absorbances less the absorbance value of the reagent blank to the mass of the analyte, nanograms, contained in the injected volume of calibration solution.

10.5.3 Net absorbance value A_A corresponds to the top 20 % of the covered mass range, and net absorbance A_B corresponds to the bottom 20 % of the covered mass range.

10.5.4 Calculate the linearity, L , as follows:

$$L = A_A/A_B \quad (7)$$

NOTE 12—The linearity compares the absorbance curve at the top 20 % of its concentration range with that of the bottom 20 % of its concentration range. Individual procedures specify the minimum ratio where relevant.

11. Keywords

11.1 characteristic mass; electrothermal atomic absorption; electrothermal atomic absorption spectrometry; graphite furnace; limit of detection; spectrometry

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