



Standard Practice for Electrothermal (Graphite Furnace) Atomic Absorption Analysis¹

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1. Scope

1.1 This practice covers a procedure for the determination of microgram per millilitre ($\mu\text{g/mL}$) or lower concentrations of elements in solution using an electrothermal atomization device attached to an atomic absorption spectrophotometer. A general description of the equipment is provided. Recommendations are made for preparing the instrument for measurements, establishing optimum temperature conditions and other criteria which should result in determining a useful calibration concentration range, and measuring and calculating the test solution analyte concentration.

1.2 *This standard does not purport to address all of the safety problems, 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.* Specific safety hazard statements are given in Section 9.

NOTE 1—This practice is a companion to Practice E 663.

2. Referenced Documents

2.1 ASTM Standards:

- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals
- E 131 Terminology Relating to Molecular Spectroscopy
- E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials²
- E 406 Practice for Using Controlled Atmospheres in Spectrochemical Analysis³
- E 416 Practice for Planning and Safe Operation of a Spectrochemical Laboratory³
- E 663 Practice for Flame Atomic Absorption Analysis³
- E 863 Practice for Describing Flame Atomic Absorption Spectroscopy Equipment³

3. Terminology

3.1 Refer to Terminology E 131 and E 135 for the definition of terms used in this practice.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *atomization*—the formation of ground state atoms that absorb radiation from a line emission source (see Practice E 663). The atomization process in electrothermal atomic absorption analysis is covered in greater detail in 6.2.

3.2.2 *pyrolysis*—the process of heating a specimen to a temperature high enough to remove or alter its original matrix, but not so high as to volatilize the element to be measured. The purpose of the pyrolysis step in electrothermal atomic absorption analysis is to remove or alter the original specimen matrix, thereby reducing or eliminating possible interferences to the formation of ground state atoms that are formed when the temperature is increased during the atomization step. Many publications and references will refer to pyrolysis as *charring* or *ashing*.

3.2.3 *pyrolytic graphite coating*—a layer of pyrolytic graphite that coats a graphite tube used in electrothermal atomic absorption analysis. Pyrolytic graphite is formed by pyrolyzing a hydrocarbon, for example, methane, at 2000°C.

3.2.4 *ramping*—a slow, controlled increase of the temperature in the graphite tube. Ramping will provide for an efficient but not too rapid removal or decomposition of the specimen matrix. Most electrothermal atomizers allow for ramping during the drying, pyrolysis, and atomization steps. It is usually employed during the drying and pyrolysis steps. However, some instrument manufacturers may recommend ramping during the atomization step depending on the specimen matrix and the element being measured (for example, the analysis of cadmium or lead in hair or blood). The power supplies for most instruments also allow the rate of the temperature increase to be varied.

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4. Significance and Use

4.1 This practice is intended for spectroscopists who are attempting to establish electrothermal atomic absorption procedures. Used in conjunction with Practice E 663, it should be helpful for establishing a complete atomic absorption analysis program.

5. Theory of Atomic Absorption Spectroscopy

5.1 Practice E 663 provides a brief discussion of the theory of flame atomic absorption spectroscopy. A more complete and detailed discussion of atomic absorption spectroscopy may be found in Dean and Rains (1).

6. Theory of Electrothermal Atomic Absorption Spectroscopy

6.1 *Basic Technique*—A discrete amount of test solution is heated in an electrothermal device to produce a cloud of neutral atoms. Light, emitted by a specific element from a line source at a specific wavelength, is passed through the cloud and neutral atoms of this same element in the cloud absorbs some of this light. Thus the intensity of the beam is decreased at the wavelengths characteristic of the element. This absorbance of radiation from the external light source depends on the population of the neutral atoms and is proportional to the concentration of the element in the test solution.

6.2 *Electrothermal Atomization Theory*—Thermodynamic and kinetic theories must be considered to fully understand the atomization process that takes place in the electrothermal atomizer. Fuller (2) and also Campbell and Ottaway (3) provide a complete discussion of the thermodynamic theory. They also discuss thermal dissociation of metal oxides, reduction of metal oxides, evaporation of metal oxides prior to atomization, and carbide formation. Several models have been proposed to explain the theory of kinetic atomization. Two studies provide a general summary of these models: one provides a discussion of atomization under increasing temperature (4), the other discusses atomization under isothermal conditions (5). Additional discussion and clarification of the kinetic atomization theory is provided by Pavari-Fontana et al (6) and Johnson et al (7).

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—Most flame atomic absorption spectrophotometers manufactured currently can be easily adapted for electrothermal analysis. These spectrophotometers are described in Practice E 863.

7.1.1 Automatic background correction is necessary for all spectrophotometers used with electrothermal devices. When electrothermal atomizers, especially graphite furnaces, are heated to high temperatures, background from absorption is produced within the graphite tube. Also, small amounts of particular matter in the furnace contribute to the background signal. Therefore, it is essential to correct or compensate for this background.

7.2 *Electrothermal Atomizers*—The most commonly used electrothermal atomizer is the graphite tube furnace. This atomizer consists of a graphite tube positioned in a water-cooled unit designed to be placed in the optical path of the

spectrophotometer so that the light from the hollow cathode lamp passes through the center of the tube. The tubes vary in size depending upon a particular instrument manufacturer's furnace design. These tubes are available with or without pyrolytic graphite coating. However, because of increased tube life, tubes coated with pyrolytic graphite are commonly used. The water-cooled unit or atomizer head which holds the graphite tube is constructed in such a way that an inert gas, usually argon or nitrogen, is passed over, around, or through the graphite tube to protect it from atmospheric oxidation. The heating of all of these atomizers is controlled by power supplies which make it possible to heat the graphite tube to 3000°C in less than 1 s. Temperatures and drying, pyrolysis, and atomization times are controlled by these power supplies (determination of these parameters are covered later in Section 10. The flow of the inert gas through the atomizer head also is controlled by the power supplies.

7.2.1 Other types of atomizers and accessories such as the graphite cup, graphite rod, L'vov platform, tantalum filament, and tantalum boat have been used and are covered in the literature. With the exception of the L'vov platform, they have not enjoyed the widespread and general use that the graphite tube atomizers have. Therefore, they will not be covered in detail within this practice. A good general description of these other units is provided by Fuller (2).

7.3 *Signal Output System*—The output signal resulting from the atomization of a specimen may be displayed by a strip chart recorder, video display, digital computer, printer, or other suitable device depending on the electronic capability of the spectrophotometer employed.

7.3.1 If a strip chart recorder is used, it must have a full scale response of 0.5 s or less. Normally, when a strip chart recorder is used, the absorption is determined by measuring the peak height of the recorder tracing. This procedure is appropriate because the absorption signal generated by an electrothermal atomizer usually results in a very narrow peak (absorption versus time). However, some specimen matrices may require instrumental parameters (for example, ramping), which will result in broad absorption versus time peaks. In such cases, peak area measurement may be more appropriate. The instrument manufacturer's manual should be consulted to determine which procedure is most suitable for the instrument being used.

8. Reagents and Materials

8.1 Picogram quantities of some elements can be determined by means of electrothermal atomization. Therefore, all acids and water used to prepare calibration solutions and test solutions shall be double distilled or ultra-pure in quality. All reagents used in the preparation of calibration solutions and test solutions shall be spectroscopically pure.

9. Hazards

9.1 *Electrical Hazards*—The power supplies for all electrothermal atomizers require high-voltage (greater than 200 V) electrical service. Refer to Practice E 416 when connecting and testing this equipment.

9.2 *Compressed Gas Hazard*—The inert or nonoxidizing atmosphere required in the atomizer head during heating cycles is usually maintained by using argon or nitrogen gas delivered

from portable gas cylinders. Practices E 406 and E 416 should be followed when handling the cylinders and connecting flow lines to the instrument.

9.3 *Chemical Hazard*—Practice E 50 should be consulted for recommendations and precautions concerning chemical hazards.

9.4 *Ventilation*—A small hood is required to carry away any toxic fumes that may result from the atomization process. See Practice E 416.

9.5 *Laboratory*—The laboratory in which the electrothermal atomizer is operated shall be kept as clean as possible. Any procedures that may produce an atmosphere that is corrosive to the instrumentation or detrimental to the analysis of the specimen should be removed from the laboratory.

9.6 *Laboratory Apparatus*—It is imperative that all laboratory apparatus and containers used in the preparation of calibration and test solutions be chemically clean. All laboratory ware, including plastic tips used on micropipets for the transfer of calibration solutions and test solutions to the graphite tube, should be acid rinsed before being used. Once laboratory ware is acid rinsed, all of the items that come in contact with analytical solutions shall be isolated from subsequent contact with fingers, clothing, bench tops, etc.

9.7 *Magnetic background correction*—If the Electrothermal (Graphite Furnace) Atomic Absorption unit is provided with a background correction that does or can produce a magnetic field, the unit should not be operated by an individual who wears, internally or externally, a medical device such as a pacemaker, that can be affected by the magnetic field, without the approval of the prescribing and/or installing physician. In addition an appropriate warning sign should warn visitors of the magnetic field.

10. Preparation of Apparatus

10.1 *Atomizer Parameters*—All electrothermal atomizers are resistance-heated by power supplies that provide individually controlled heating stages for drying, pyrolysis, and atomization. The means to control the times and temperatures of these stages will vary with instrumentation. Most manufacturers provide a listing of the atomizer parameters required for the electrothermal analysis of numerous elements in the most commonly encountered matrices. The recommended atomizer parameters for a particular element should be verified for the specific instrument being used with an appropriate solution. Also, for sample matrices that differ from those printed in the manufacturer's list, the most appropriate time and temperature setting for each stage must be calculated or determined experimentally (see 10.1.1, , and).

NOTE 2—Ramping is normally used during the drying and pyrolysis stages. Some procedures may also recommend that ramping be used during the atomization stage, depending upon the specimen matrix and the element being measured. Refer to the instrument manufacturer's manual of the particular instrument for the recommended ramp rates, if any, for the type of solution being analyzed.

10.1.1 *Drying*—The drying stage is a low temperature stage in which the graphite tube is heated to a temperature high enough to evaporate, but not boil, any solvent. The ideal drying temperature would be one just below the boiling point of the solvent. Specimen spattering may occur if the temperature is

raised above the boiling point before evaporation is complete. The time, in seconds, required to completely dry a specimen may be calculated by multiplying 1.5 to 2 times the volume of the specimen, measured in microlitres (μL) (2). For example, a 10- μL specimen would require a drying time of 15 to 20 s (see when the highest temperature during the atomization cycle has been reached. If an auto-sampling device is to be used, adjust it to deposit the desired volume (in microlitres) in the graphite tube (see Note 3). Deposit a measured amount of the reagent blank solution, prepared as directed in 11.1, in the graphite tube. The volume should be the same as will be used for the test solution (see Note 3). Run through the heating stages and adjust the readout system of the instrument to read zero absorbance during the atomization of the reagent blank solution. If the spectrophotometer has an auto-zero capability, the auto-zero should be activated at this time. Atomize a calibration solution, prepared as directed in 11.3, containing the analyte at a concentration that will yield an absorbance of 0.1 to 0.3 and is anticipated to be within the linear absorbance range of the procedure. Where applicable, refer to the instrument manufacturer's instruction manual to determine an approximation of the linear concentration range for the analyte. Determine if adequate sensitivity ($\mu\text{g}\cdot\text{mL}^{-1}/0.0044$ absorbance) has been obtained by reference to the instrument instruction manual or to the analytical procedure that is being used.

NOTE 3—The appropriate volume, in microlitres, of any solution deposited in a graphite tube may vary depending on the sensitivity of the element being measured, the matrix of the specimen, and the expected concentration of the element being measured. The matrix blank may be substituted for the reagent blank if interference from the matrix of the test solution is expected. The instrument manufacturer's manual provides suggested volumes to be used for specific elements and matrices. These volumes can be increased or decreased, depending on the absorbance readings obtained in a preliminary check of the test specimen (see 10.1).

10.2 *Precision of Measurements*—The procedure used to determine the acceptability of instrument precision is the same as described in Practice E 663 with the following exception. If the relative standard deviation of the readings made on the calibration solution is greater than 10 %, determine the cause of the variability (for example, loss of pyrolytic graphite coating from the graphite tube) and rectify it. When an auto-sampling device is used, relative standard deviations of less than 10 % can be expected.

NOTE 4—When the specimen is deposited manually with microlitre pipets, care must be taken to deposit the specimen in exactly the same way each time, otherwise inconsistent results will be obtained.

11. Preparation of Blank and Calibration Solutions

11.1 *Reagent Blank Solution*—Combine all acids, reagents, and other additions present in the test solution and dilute to the same concentration as the test solution. This solution is used to set the zero absorbance or 100 % transmittance of the atomic absorption spectrophotometer. The reagent blank is also used as the zero point of the calibration curve. Some publications and references may refer to the reagent blank solution as the *reference solution*.

NOTE 5—If impurities in acids, reagents and other materials used to make up the reagent blank solution cause a measurable amount of the

analyte to be present in it, refer to Practice E 663.

11.2 *Matrix Blank Solution*—Combine all acids, reagents, and other additions present in the test solution. To the extent that they are known, add all of the specimen matrix elements of significant concentration, except the analyte, in the same concentrations as in the test solution. Dilute to the same concentration as the test solution. The matrix blank solution may be used to determine to what extent, if any, the matrix of the test solution will affect the absorbance of the analyte (see Note 5).

11.3 *Calibration Solutions*—Prepare a minimum of five calibration solutions to cover a concentration range that will produce an absorbance of 0.01 to 1.0 or greater (1.3 to 90 % absorption or greater). The matrix of these calibration solutions should match, as closely as possible, the matrix of the test solutions. If the composition of the test solution is unknown to the extent that matching calibration solutions cannot be prepared, use the method of standard additions described in Practice E 663.

NOTE 6—The concentration range of calibration solutions shall be determined as directed in Practice E 663.

12. Procedure

12.1 The procedure for electrothermal atomic absorption analysis is the same as that for flame atomic absorption, which is described in Practice E 663. The only difference is to

substitute the word *atomize* for the word *aspirate* whenever it appears in Practice E 663.

13. Precision and Bias

13.1 *Precision*—Precision in terms of relative standard deviation (*RSD*) will show considerable variation, depending on the element being determined, the concentration level, and the sample matrix. Other factors that may affect precision are the particular furnace configuration of a specific instrument and the use of automatic samplers. At the milligram-per-litre and microgram-per-litre levels, relative standard deviations can be expected to have a normal range of 4 to 7 %. There are reports in the literature, however, of relative standard deviations ranging from less than 1 % to greater than 10 % (). It is important, therefore, that each laboratory establish individual precision values for the particular instrument/furnace combination being used. Once these values are established, it is the responsibility of each laboratory to determine their adequacy for the analysis of specific materials.

13.2 *Bias*—An indication of the bias may be obtained by analyzing a certified reference material and comparing the values obtained with the certified values.

14. Keywords

14.1 atomic absorption; electrothermal atomization; flameless atomic absorption; graphite furnace

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