



Designation: **E1184 – 10 (Reapproved 2016) E1184 – 21**

Standard Practice for Determination of Elements by Graphite Furnace Atomic Absorption Spectrometry¹

This standard is issued under the fixed designation E1184; 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 a procedure for the determination of microgram per millilitre/milliliter ($\mu\text{g/mL}$) or lower concentrations of elements in solution using a graphite furnace attached to an atomic absorption spectrometer. 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 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific safety hazard statements are given in Section 9.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

[D1193 Specification for Reagent Water](#)

[E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials](#)

[E131 Terminology Relating to Molecular Spectroscopy](#)

[E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials](#)

[E406 Practice for Using Controlled Atmospheres in Atomic Emission Spectrometry](#)

[D1193 Specification for Reagent Water](#)

3. Terminology

3.1 Refer to Terminologies [E131](#) and [E135](#) for the definition/definitions of terms used in this practice.

3.2 *Definitions of Terms Specific to This Standard:*

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 on 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.

3.2.1 *atomization*—*atomization, v*—the formation of ground state atoms that absorb radiation from a line emission source. The atomization process in graphite furnace atomic absorption spectrometry (GF-AAS) analysis is covered in 6.2.

3.2.2 *pyrolysis*—*pyrolysis, n*—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 GF-AAS 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*—*coating, n*—a layer of pyrolytic graphite that coats a graphite tube used in GF-AAS analysis. Pyrolytic graphite is formed by pyrolyzing a hydrocarbon, for example, methane, at 2000 °C.

3.2.4 *ramping*—*ramping, v*—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 graphite furnaces 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.

4. Significance and Use

4.1 This practice is intended for users who are attempting to establish GF-AAS procedures. It should be helpful for establishing a complete atomic absorption analysis program.

5. Theory of Atomic Absorption Spectrometry (AAS)

5.1 In flame atomic absorption spectrometry (Flame-AAS), a test solution is aspirated into a flame through which passes radiation from a line emission source of the element sought. The radiation of the element sought is absorbed in proportion to the concentration of its neutral atoms present in the flame. The concentration of the analyte is obtained by comparison to calibrations.

5.2 The theoretical basis for using atomic absorption to determine analyte concentration can be found in texts on instrumental analysis in analytical chemistry and in the literature.

6. Theory of Graphite Furnace Atomic Absorption Spectrometry

6.1 *Basic Technique*—A discrete amount of test solution is heated in a graphite furnace 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 absorb 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 *Graphite Furnace Atomization*—Thermodynamic and kinetic theories must be considered to fully understand the atomization process that takes place in the graphite furnace. Jackson (1)³ and also Campbell and Ottaway (2) 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. A search of the literature will find discussions of atomization under increasing temperature, and atomization under isothermal conditions (3). Additional discussion and clarification of the kinetic atomization theory is provided by Paveri-Fontana et al. (4).

7. Apparatus

7.1 *Atomic Absorption Spectrometer*—Most flame atomic absorption spectrometers manufactured currently can be easily adapted for graphite furnace analysis.

³ The boldface numbers in parentheses refer to a list of references at the end of this standard.

7.1.1 Automatic background correction is necessary for all spectrometers used with graphite furnaces. When graphite furnaces are heated to high temperatures, background from absorption is produced within the graphite tube. Also, small amounts of particulate 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 spectrometer 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~~ 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 is 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 can be found in the literature.

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 spectrometer 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 a graphite furnace 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 graphite furnace atomization. Therefore, ultra-pure acids and Type I (Specification **D1193**) water shall be used to prepare calibration solutions and test solutions.

9. Hazards

9.1 *Electrical Hazards*—The power supplies for graphite furnaces require high-voltage (greater than 200 V) electrical service. Electrical power shall be supplied as determined from load requirements in accordance with the latest revision of the National Electrical Code. The recommendations of the equipment manufacturers and local engineers should be followed in designing the electrical service.

9.2 *Compressed Gas Hazard*—The inert or non-oxidizing atmosphere required in the graphite furnace during heating cycles is usually maintained by using argon or nitrogen gas delivered from portable gas cylinders.

9.2.1 Sufficient space shall be provided for the cylinders, which shall be kept in a vertical position and always well secured. They shall not be used or stored near burners, hot plates, or in any area where the temperature exceeds 52 °C (125 °F). The contents shall be identified with labels or stencils and color coding.

9.2.2 Two-stage regulators with pressure gages should be used as part of the basic flow system to deliver required cylinder gas to the instrument at a reduced pressure. Practice **E406** and the manufacturer's instructions should be followed with regard to the types of regulators, flow-metering valves, and tubing for gas transport when designing a gas delivery system.

9.2.3 Reserve gas cylinders should not be stored in the laboratory area. Gas storage areas shall be adequately ventilated, fire-resistant, located away from sources of ignition or excessive heat, and dry. All cylinders shall be chained in place or placed in partitioned cells to prevent them from falling over. In all cases, storage areas shall comply with local, state, and municipal

requirements as well as with the standards of the Compressed Gas Association and the National Fire Prevention Association. Access to gas storage areas should be limited to authorized personnel.

9.3 *Chemical Hazard*—Practice **E50** 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. Follow the manufacturer’s instructions for proper hood installation.

9.5 *Laboratory*—The laboratory in which the graphite furnace 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 acid cleaned. 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 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 or installing physician, or both. In addition an appropriate warning sign should warn visitors of the magnetic field.

10. Preparation of Apparatus

10.1 *Graphite Furnace Parameters*—All graphite furnaces 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 parameters required for the graphite furnace analysis of numerous elements in the most commonly encountered matrices. The recommended 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**).

iTeh Standards

ASTM E1184-21

<https://standards.itih.ai/catalog/standards/sist/26ed3c04-94ed-4bb8-9b69-ccacbec97300/astm-e1184-21>

NOTE 1—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 times to 2 times the volume of the specimen, measured in ~~microlitres~~microliters (μL). For example, a 10-μL specimen would require a drying time of 15 s to 20 s. If an auto-sampling device is to be used, adjust it to deposit the desired volume (in ~~microlitres~~microliters) in the graphite tube (see **Note 2****10.1.2**). Deposit a measured amount of the reagent blank solution, prepared as directed in **11.1**, in the graphite tube. The volume should be identical to the test solution volume (see **Note 2****10.1.2**). Cycle 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 spectrometer 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 ($\mu\text{g}\cdot\text{mL}(\mu\text{g}\cdot\text{mL}/0.0044^{-1}/0.0044$ absorbance) has been obtained by reference to the instrument instruction manual or to the analytical procedure utilized.

NOTE 2—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**).

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10.2 *Precision of Measurements*—Use the following procedure to determine if the instrument precision is acceptable. Set the absorbance reading to zero as in 10.1.1. Obtain an absorbance reading on a calibration solution that will yield an absorbance reading of 0.2 to 0.4. Repeat the measurement sequence for the reagent blank and calibration solutions to obtain six readings of absorbance for the calibration solution. Calculate the *standard deviation* of the readings made on this calibration solution by applying acceptable statistical methods. 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 3—When the specimens are deposited manually with microlitre pipets, care must be taken to deposit the specimens in exactly the same way every time; otherwise, inconsistent results will be obtained.

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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~~ volume as the test solution. This solution is used to set the zero absorbance or 100 % transmittance of the atomic absorption spectrometer. 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 4—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, the blank absorbance reading must be converted to concentration of the analyte in the calibration solutions, when these solutions are used to establish the useful calibration range. When the calibration solutions are used to construct a working curve to measure the analyte in the test solution, the blank concentration may be subtracted from the analyte concentration or added to the calibration concentrations as directed by the basic method.

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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,~~ elements, except the analyte, in the same concentrations as in the test solution. Dilute to the same ~~concentration~~ volume 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 4** 11.1.1).

11.3 *Calibration Solutions*—Prepare calibration solutions to cover a concentration range that will produce an absorbance reading 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 13.5. If using the low concentration method described in 13.4, to prevent contamination and carryover, the highest calibration solution should have an absorbance reading between 0.2 and 0.4.

NOTE 2—The concentration range of calibration solutions shall be determined as directed in Section 12.

11.4 *Matrix Modifiers*—Use of matrix modifiers should be investigated for the analyte determination being made. Matrix modifiers may chemically alter the matrix or analyte in order to change their response to thermal conditions in the furnace. When a modifier

is used, the analyte may become more thermally stable allowing a higher ashing temperature or the matrix may become more volatile allowing a lower charring temperature. The literature, including instrument manufacturer’s application information, provides guidance to the matrix modifiers typically used for determination of a particular analyte. The matrix modifier is typically added directly to the furnace coincident with the introduction of the blank, calibration, or sample solutions.

12. Determination of Useful Concentration Range

12.1 *General Considerations*—The useful concentration range for a particular analytical system must be determined experimentally because the useful range will depend on the operation and characteristics of the individual instrument. Three different approaches to the determination of this useful range are described in 12.2, 12.3, and 12.4. Selection of the approach to be used depends on the precision requirements of the analytical method, or the limitations of the instrument used, or the concentration range of the analyte in the material to be analyzed, or all three.

12.1.1 For any of the three approaches, prepare a reference solution as directed in 11.1 and calibration solutions as directed in 12.1.2. Prepare the GF-AAS and adjust the readout system to zero absorbance as directed in 10.1.1 using the reference solution. Atomize the calibration solutions in the order recommended by the manufacturer or directed by the basic method, and measure the absorbance as directed in 12.2, 12.3, and 12.4. If the instrument has a time-integration feature, use at least a 2-s integration period. At the lower absorbance readings, use scale expansion to obtain at least two, and preferably, three significant figures in the absorbance reading.

12.1.2 Using the manufacturer’s data as a guide and some trial and error, prepare a minimum of twelve calibration solutions to cover the absorbance range 0.005 to 1.5, or greater if needed. At least three of these solutions should be in the absorbance range 0.005 to 0.1 and three in the absorbance range 0.9 to 1.5. The remaining six solutions should be approximately equally spaced in terms of concentration between 0.1 absorbance and 0.9 absorbance. These calibration solutions should, as closely as possible, match the composition of the test solution. If the composition of the test solution is unknown to the extent that matching calibration solutions cannot be prepared, refer to the method of standard additions described in 13.5.

12.2 *Rigorous Determination of Useful Concentration Range*—If rigorous determination (5, 6) of the low and high limits of the useful concentration range is required due to the precision requirements of the analytical method or the limitations of GF-AAS, or both, use this approach. Take six measurements of absorbance as directed in 12.1.1 on each of the calibration solutions described in 11.1 and 12.1.2. Average the absorbance readings and calculate the *estimated standard deviation* (s_A) of the absorbance readings for each set of absorbance measurements for each calibration solution. Plot a calibration curve of the average absorbance readings against concentration. Draw a smooth curve through the points and inspect visually for any obvious anomalies. If any are present, determine the cause and correct. From the (s_A) of the absorbance readings for each calibration solution, calculate its *relative concentration equivalent* (RCE) as follows:

$$RCE = 100 \times \left[\frac{(C_2 - C_1)}{(A_2 - A_1)} \right] \left[\frac{s_A}{C_2} \right] \quad (1)$$

Where:

- C_1 = the lower of two adjacent concentrations,
- C_2 = the higher of two adjacent concentrations,
- A_1 = absorbance reading for C_1 ,
- A_2 = absorbance reading for C_2 , and
- s_A = estimated standard deviation for A_2 .

Plot RCE against concentration as shown in Fig. 1. Select the useful range in terms of the relative precision requirements of the analytical method. If, for example, a single measurement relative precision of 1 % or better is required, Instrument 1 will have a useful range of 5 µg/mL to 130 µg/mL, but Instrument 2 would not qualify without additional replication. However, if the relative precision requirement is relaxed to 2 %, then Instrument 2 will qualify with single measurements and will have a useful range of 15 µg/mL to 85 µg/mL.

NOTE 3—If a conservative cross check on this approach to the useful range is desired, process the average absorbance values as directed in 12.3.

12.3 *Conservative Determination of Useful Concentration Range*—If a rigorous determination of the high and low limits of the useful concentration range is not required, this conservative approach may be used and will require substantially fewer measurements (7-9). Make a single measurement of transmittance for each of the calibration solutions in 11.1 and 12.1.2. If only

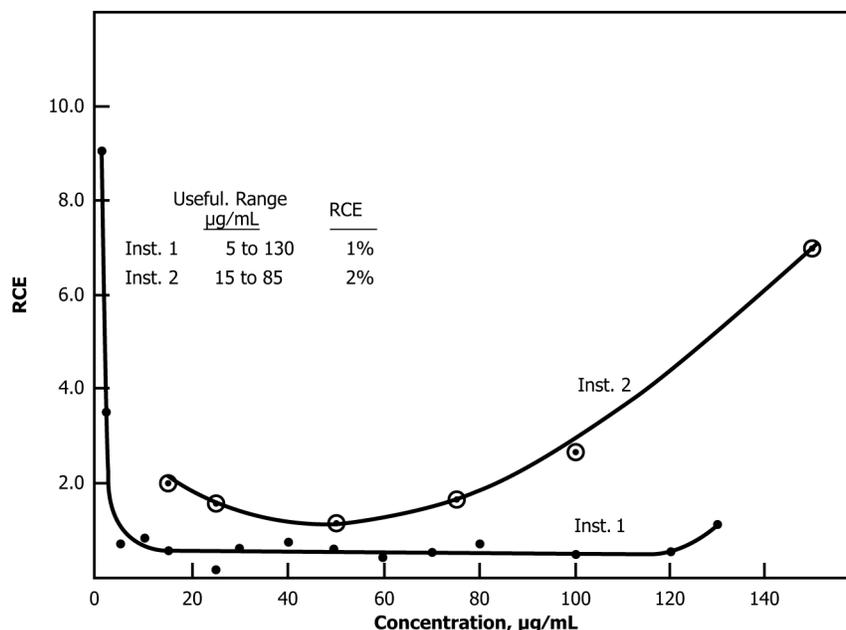


FIG. 1 RCE Versus Concentration (Lead in 2 % HNO₃, 283.3-nm Line)

absorbance can be measured on the instrument or is available from other measurements, convert each absorbance measurement to percent transmittance by means of the relationship:

$$A = \log_{10} \left(\frac{100}{T} \right) \tag{2}$$

Where:

A = absorbance, and

T = transmittance expressed as a %.

Make two plots, one of % T against the log₁₀ concentration of the analyte, the other of (% T)^{1/2} against the log₁₀ concentration of the analyte. If the instrument has a photo-conductive detector (7) and errors due to scale reading and dark current drift are dominant, then the first plot, Curve 1 of Fig. 2, defines the low and high ends of the useful range. These are the points at which the curve departs from linearity. Thus, the low end of the range is given by A and the high end of the range by B, or a concentration range of 5 µg/mL to 40 µg/mL. If the instrument has a photomultiplier detector and errors due to shot noise are dominant, Curve 2, the (% T)^{1/2} plot, applies. The high end of the useful concentration range is given by C. The low end according to the theory should be D but the experimental evidence available shows that point A on Curve 1 is a better choice. Accordingly, for the latter-type instrument the useful concentration range is defined by A on Curve 1 and C on Curve 2, or a concentration range of 5 µg/mL to 90 µg/mL.

12.4 Combination Determination of Useful Concentration Range—If rigorous measurement of only one of the useful concentration range limits is needed, make six measurements of absorbance, as directed in 12.2, on each of enough calibration solutions to define this limit. Process and plot these data as directed in 12.2 for selection of the required useful range limit. On each of the remaining solutions of the twelve, make single measurements of % T and process these data as directed in 12.3 to define the other limit of the useful range.

NOTE 7—If maximum precision is not required, the useful concentration range may be lowered or increased provided the precision satisfies the specifications of the analytical method. Extending the useful concentration range may be necessary, particularly at the trace concentration level, where method development to control the concentration of the analyte to fall within the useful concentration range may be difficult or impractical.

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