



Designation: E 60 – 98

Standard Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry¹

This standard is issued under the fixed designation E 60; 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 general recommendations for photoelectric photometers and spectrophotometers and for photometric practice prescribed in ASTM methods for chemical analysis of metals, sufficient to supplement adequately the ASTM methods. A summary of the fundamental theory and practice of photometry is given. No attempt has been made, however, to include in this practice a description of every apparatus or to present recommendations on every detail of practice in ASTM photometric or spectrophotometric methods of chemical analysis of metals.²

1.2 These recommendations are intended to apply to the ASTM photometric and spectrophotometric methods for chemical analysis of metals when such standards make definite reference to this practice, as covered in Section 4.

1.3 In this practice, the terms “photometric” and “photometry” encompass both filter photometers and spectrophotometers, while “spectrophotometry” is reserved for spectrophotometers alone.

1.4 *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 131 Terminology Relating to Molecular Spectroscopy³
- E 168 Practices for General Techniques of Infrared Quantitative Analysis³
- E 169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis³
- E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers³

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 E01.20 on Fundamental Practices and Measurement Traceability.

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² For additional information on the theory and photoelectric photometry, see the list of references at the end of this practice.

³ *Annual Book of ASTM Standards*, Vol 03.06.

3. Terminology Definitions and Symbols

3.1 For definitions of terms relating to absorption spectroscopy, refer to Terminology E 131.

3.2 *background absorption*—any absorption in the solution due to the presence of absorbing ions, molecules, or complexes of elements other than that being determined is called background absorption.

3.3 *concentration range*—the recommended concentration range shall be designated on the basis of the optical path of the cell, in centimetres, and the final volume of solution as recommended in a procedure. In general, the concentration range and path length shall be specified as that which will produce transmittance readings in the optimum range of the instrument being used as covered in Section 14.

3.4 *initial setting*—the initial setting is the photometric reading (usually 100 on the percentage scale or zero on the logarithmic scale) to which the instrument is adjusted with the reference solution in the absorption cell. The scale will then read directly in percentage transmittance or in absorbance.

3.5 *photometric reading*—the term “photometric reading” refers to the scale reading of the instrument being used. Available instruments have scales calibrated in transmittance, T , (1)⁴ or absorbance, A , (2) (see 5.2), or even arbitrary units proportional to transmittance or absorbance.

3.6 *reagent blank*—the reagent blank determination yields a value for the apparent concentration of the element sought, which is due only to the reagents used. It reflects both the amount of the element sought present as an impurity in the reagents, and the effect of interfering species.

3.7 *reference solution*—photometric readings consist of a comparison of the intensities of the radiant energy transmitted by the absorbing solution and the radiant energy transmitted by the solvent. Any solution to which the transmittance of the absorbing solution of the substance being measured is compared shall be known as the reference solution.

4. Reference to This Practice in Standards

4.1 The inclusion of the following paragraph, or a suitable equivalent, in any ASTM test method (preferably after the

⁴ The boldface numbers in parentheses refer to the list of references appended to this practice.

section on scope) shall constitute due notification that the photometers, spectrophotometers, and photometric practice prescribed in that test method are subject to the recommendations set forth in this practice.

*“Photometers, Spectrophotometers, and Photometric Practice—Photometers, spectrophotometers, and photometric practice prescribed in this test method shall conform to ASTM Practice E 60, Photometric and Spectrophotometric Methods for Chemical Analysis of Metals.”*⁵

5. Theory

5.1 Photoelectric photometry is based on Bouguer’s and Beer’s (or the Lambert-Beer) laws which are combined in the following expression:

$$P = P_o 10^{-abc}$$

where:

P = transmitted radiant power,

P_o = incident radiant power, or a quantity proportional to it, as measured with pure solvent in the beam,

a = absorptivity, a constant characteristic of the solution and the frequency of the incident radiant energy,

b = internal cell length (usually in centimetres) of the column of absorbing material, and

c = concentration of the absorbing substance, g/L.

5.2 Transmittance, T , and absorbance, A , have the following values:

$$T = P/P_o$$

$$A = \log_{10} (1/T) = \log_{10} (P_o/P)$$

where P and P_o have the values given in 5.1.

5.3 From the transposed form of the Bouguer-Beer equation, $A = abc$, it is evident that at constant b , a plot of A versus c gives a straight line if Beer’s law is followed. This line will pass through the origin if the usual practice of cancelling out solvent reflections and absorption and other blanks is employed.

5.4 In photometry it is customary to make indirect comparison with solutions of known concentration by means of calibration curves or charts. When Beer’s law is obeyed and when a satisfactory instrument is employed, it is possible to dispense with the curve or chart. Thus, from the transposed form of the Bouguer-Beer law, $c = A/ab$, it is evident that once a has been determined for any system, c can be obtained, since b is known and A can be measured.

5.5 The value for a can be obtained from the equation $a = A/cb$ by substituting the measured value of A for a given b and c . Theoretically, in the determination of a for an absorbing system, a single measurement at a given wavelength on a solution of known concentration will suffice. Actually, however, it is safer to use the average value obtained with three or more concentrations, covering the range over which the determinations are likely to be made and making several readings at each concentration. The validity of the Bouguer-Beer law for a particular system can be tested by showing that a remains constant when b and c are changed.

6. General Requirements for Photometers and Spectrophotometers

6.1 A photoelectric photometer consists essentially of the following:

NOTE 1—The choice of an instrument may naturally be based on price considerations, since there is no point in using a more elaborate (and, incidentally, more expensive) instrument than is necessary. In addition to satisfactory performance from the purely physical standpoint, the instrument should be compact, rugged enough to stand routine use, and not require too much manipulation. The scales should be easily read, and the absorption cells should be easily removed and replaced, as the clearing, refilling, and placing of the cells in the instrument consume a major portion of the time required. It is advantageous to have an instrument that permits the use of cells of different depth (see Recommended Practice E 275).

6.1.1 An illuminant (radiant energy source),

6.1.2 A device for selecting relatively monochromatic radiant energy (consisting of a diffraction grating or a prism with selection slit, or a filter),

6.1.3 One or more absorption cells to hold the sample, standards, reagent blank, or reference solution, and

6.1.4 An arrangement for photometric measurement of the intensity of the transmitted radiant energy, consisting of one or more photocells or photosensitive tubes, and suitable devices for measuring current or potential.

6.2 Precision instruments that employ monochromators capable of supplying radiant energy of high purity at any chosen wavelength within their range are usually referred to as spectrophotometers. Instruments employing filters are known as filter photometers or abridged spectrophotometers, and usually isolate relatively broad bands of radiant energy. In most cases the absorption peak of the compound being measured is relatively broad, and sufficient accuracy can be obtained using a fairly broad band (10 to 75 nm) of radiant energy for the measurement (Note 2). In other cases the absorption peaks are narrow, and radiant energy of high purity (1 to 10 nm) is required. This applies particularly if accurate values are to be obtained in those systems of measurement based on the additive nature of absorbance values.

NOTE 2—One nanometre (nm) equals one millimicron (m μ).

7. Types of Photometers and Spectrophotometers

7.1 *Single-Photocell Instruments*—In most single-photocell instruments, the radiant energy passes from the monochromator or filter through the reference solution to a photocell. The photocurrent is measured by a galvanometer or a microammeter and its magnitude is a measure of the incident radiant power, P_o . An identical absorption cell containing the solution of the absorbing component is now substituted for the cell containing the reference solution and the power of the transmitted radiant energy, P , is measured. The ratio of the current corresponding to P to that of P_o gives the transmittance, T , of the absorbing solution, provided the illuminant and photocell are constant during the interval in which the two photocurrents are measured. It is customary to adjust the photocell output so that the galvanometer or microammeter reads 100 on the percentage scale or zero on the logarithmic scale when the

⁵ Annual Book of ASTM Standards, Vol 03.05.

incident radiant power is P_o , in order that the scale will read directly in percentage transmittance or absorbance. This adjustment is usually made in one of three ways. In the first method, the position of the cross-hair or pointer is adjusted electrically by means of a resistance in the photocell-galvanometer circuit. In the second method, adjustment is made with the aid of a rheostat in the source circuit (Note 3). The third method of adjustment is to control the quantity of radiant energy striking the photocell with the aid of a diaphragm somewhere in the path of radiant energy.

NOTE 3—Kortüm (3) has pointed out on theoretical grounds this method of controls is faulty, since the change in voltage applied to the lamp not only changes the radiant energy emitted but also alters its chromaticity. Actually, however, instruments employing this principle are giving good service in industry, so the errors involved evidently are not too great.

7.2 Two-Photocell Instruments—In order to eliminate the effect of fluctuation of the source, a great many types of two-photocell instruments have been proposed. Most of these are good, but some have poorly designed circuits and do not accomplish the purpose for which they are designed. Following is a brief description of two types of two-photocell photometers and spectrophotometers that have been found satisfactory:

7.2.1 In the first type of two-photocell instrument, beams of radiant energy from the same source are passed through the reference solution and the sample solution and are focused on their respective photocells. Prior to insertion of the sample, the reference solution is placed in both absorption cells, and the photocells are balanced with the aid of a potentiometric bridge circuit (Note 4). The reference solution and sample are then inserted and the balance reestablished by manipulation of the potentiometer until the galvanometer again reads zero. By choosing suitable resistances and by using a graduated slide wire, the scale of the latter can be made to read directly in transmittance. It is important that both photocells show linear response, and that they have identical radiation sensitivity if the light is not monochromatic.

NOTE 4—Since b is defined as the internal cell length, the cancellation of radiant energy lost at the glass-liquid interfaces and within the glass must be accomplished by inserting the reference solution in the absorption cells.

7.2.2 The second type of two-photocell instrument is similar to the first, except that part of the radiant energy from the source is passed through an absorption cell to the first photocell; the remainder is impinged on the second photocell without, however, passing through an absorption cell. Adjustment of the calibrated slide wire to read 100 on the percentage scale, with the reference solution in the cell, is accomplished by rotating the second photocell. The reference solution is then replaced by the sample and the slide wire is turned until the galvanometer again reads zero.

8. Radiation Source

8.1 In most of the commercially available instruments the illuminant is an incandescent lamp with a tungsten filament. This type of illuminant is not ideal for all work. For example, when an analysis calls for the use of radiant energy of wavelengths below 400 nm, it is necessary to maintain the

filament at as high a temperature as possible in order to obtain sufficient radiant energy to ensure the necessary sensitivity for the measurements. This is especially true when operating with a photovoltaic cell, for the response of the latter falls off quickly in the near ultraviolet. The use of high-temperature filament sources may lead to serious errors in photometric work if adequate ventilation is not provided in the instrument in order to dissipate the heat. Another important source of error results from the change of the shape of the energy distribution curve with age. As a lamp is used, tungsten will be vaporized and deposited on the walls. As this condensation proceeds, there is a decrease in the radiation power emitted and, in some instances, a change in the composition of the radiant energy. This change is especially noticeable when working in the near ultraviolet range and will lead to error (unless frequent standardization is resorted to) in all except those cases where essentially monochromatic radiant energy is used.

NOTE 5—The errors discussed in 8.1 have been successfully overcome in commercially available instruments. One instrument has been so designed that a very low-current lamp (of the order of 200 mA) is employed as the source. This provides for long lamp life, freedom from line fluctuations (since a storage battery is employed), stability of energy distribution, reproducibility, and low-cost operation. In addition, the stable illuminant permits operation for long periods of time without need for restandardization against known solutions.

8.2 In most of the commercially available instruments where relatively high-wattage lamps are used, the power is derived from the ordinary electric mains with the aid of a constant-voltage transformer. Where the line voltages vary markedly, it is necessary to resort to the use of batteries that are under continuous charge, or to a very good constant voltage regulator.

9. Filters and Monochromators

9.1 Filters—Relatively inexpensive instruments employing filters are adequate for a large proportion of photometric methods, since most absorbing systems show broad absorption bands. In general, filters are designed to isolate as narrow a band of the spectrum as possible. Actually, it is usually necessary, especially when the filters are to be used in conjunction with an instrument employing photovoltaic cells, to sacrifice spectral purity in order to obtain sufficient sensitivity for measurement with a rugged galvanometer or a microammeter. Glass filters are most often used because of their stability to light and heat, but gelatin filters and even aqueous solutions are sometimes used.

9.2 Monochromators—Spectrophotometric methods call for the isolation of more or less narrow wavebands of radiant energy. Two types of monochromators are in common use: the prism and the diffraction grating. Prisms have the disadvantage of exhibiting a dependence of dispersion upon wavelength. On the other hand, the elimination of stray radiation energy is less difficult when a prism is used. In a well-designed monochromator, stray radiant energy resulting from reflections from optical and mechanical members is reduced to a minimum, but some radiant energy, caused by nonspecular scatterings by the optical elements, will remain. This unwanted radiant energy can be reduced through the use of a second monochromator or a filter in combination with a monochromator. Unfortunately,