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Standard Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry¹

This standard is issued under the fixed designation E60; 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:*³

E131 Terminology Relating to Molecular Spectroscopy

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E168 Practices for General Techniques of Infrared Quantitative Analysis

E169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Definitions and Symbols

3.1 For definitions of terms relating to this practice, refer to Terminology **E135**.

3.2 For definitions of terms relating to absorption spectroscopy, refer to Terminology **E131**.

3.3 *Definitions of Terms Specific to this Practice:*

3.3.1 *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.

3.3.2 *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.

3.3.3 *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.

3.3.4 *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.

3.3.5 *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.

⁴ The boldface numbers in parentheses refer to a list of references at the end of 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 additional information on the theory and photoelectric photometry, see the list of references at the end of this practice.

³ 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.

3.3.6 *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 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 E60, Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry.

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 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. 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.

APPARATUS

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 Practice E275).

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, calibration, reagent blank, or reference solutions, 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. Frequently the absorption peak of the compound being measured is relatively broad, and sufficient accuracy can be obtained using a fairly broad band (10 nm to 75 nm) of radiant energy for the measurement (Note 2). Other times the absorption peaks are narrow, and radiant energy of high purity (1 nm 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 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 controls 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 noted 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 excessive.

7.2 Two-Photocell Instruments—To eliminate the effect of fluctuation of the source, 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. 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. 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.

7.2.2 The second type of two-photocell instrument is similar to the first, but 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 calibration is performed) in all except those cases where essentially monochromatic radiant energy is used.

NOTE 4—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 (approximately 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 repeated calibrations 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 stable 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. 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 fairly 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. However, 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, any process of monochromatization is accompanied by a reduction of the radiant power, and the more complex the monochromator the greater the burden upon the measuring system.

10. Absorption Cells

10.1 Some photometers and spectrophotometers provide for the use of several sizes and shapes of absorption cells. Others are designed for a single type of cell. It is advantageous to have an instrument that permits the use of cells of different depths. In some single-photocell instruments there is only one receptacle for the cell; in others (and this is especially desirable in those instruments where the illuminant is unstable) a sliding carriage is provided so that two cells can be interchangeably inserted into the beam of radiant energy coming from the monochromator.

11. Photocells and Photosensitive Tubes

11.1 In photometry, the measurement of radiant energy is usually accomplished with the aid of either photoemission or photovoltaic cells.

11.2 The spectral response of a photoemission cell will depend upon the alkali metal employed and upon its treatment during manufacture. The spectral response of a photovoltaic (or barrier-layer) cell is crudely similar to that of the human eye, except that it extends from about 300 nm to 700 nm. In general, neither the voltage nor the current response of a photovoltaic cell is a linear function of the flux incident on the cell, but the current response is more linear than the voltage response. Thus, current-measuring devices should be used with photovoltaic-cell instruments. The degree to which the response of these cells departs from linearity depends on the individual cell, its temperature, its level of illumination, the geometric distribution of this illumination on its face, and the resistance of the current-measuring circuit.

11.3 For a photocell to be useful, it must exhibit a constancy of current with time of exposure. Most commercial alkali cells currently in use produce a constant current after an exposure of a few minutes. The photovoltaic cells, however, frequently exhibit enough reversible fatigue to interfere with their use. The measures which improve linearity of response also tend to reduce fatigue. With most commercial instruments, the errors due to reversible fatigue are usually less than 1 %.

12. Current-Measuring Devices

12.1 The usual types of photometers and spectrophotometers employ photovoltaic cells in conjunction with a microammeter or a moderately high-sensitivity galvanometer, as may be appropriate for the illumination level employed. The scales for the galvanometers are sometimes designed to permit reading of absorbance values but more often yield only the more conveniently read T or percentage T values. Some photometers and

spectrophotometers are designed so that the current is measured potentiometrically, using the galvanometer as a null instrument. It is stated that the error due to nonlinearity of the galvanometer under load is eliminated. However, this error is usually small and many instruments provide individual calibration of the galvanometer.

12.2 When photoemission cells are used, current amplification is usually performed before the galvanometer or meter is used.

PHOTOMETRIC PRACTICE

13. Principle of Test Method

13.1 Photometric methods are generally based on the measurement of the transmittance or absorbance of a solution of an absorbing salt, compound, or reaction product of the substance to be determined. It is usually desirable to perform a rather complete photometric investigation of the reaction before attempting to employ it in quantitative analysis (see Practices E168 and E169). The investigation should include a study of the following:

13.1.1 The specificity of any reagent employed to produce absorption,

13.1.2 The validity of Beer's law,

13.1.3 The effect of salts, solvent, pH, temperature, concentration of reagents, and the order of adding the reagents,

13.1.4 The time required for absorption development and the stability of the absorption,

13.1.5 The absorption curve of the reagent and the absorbing substances, and

13.1.6 The optimum concentration range for quantitative analysis.

13.2 In photometry it is necessary to ascertain the spectral region for use in the determination. In general it is desirable to use a filter or monochromator setting such that the isolated spectral portion is in the region of the absorption maximum. Ideally (and, fortunately, this is true of most of the absorbing systems encountered in quantitative inorganic analysis) the absorption maximum is quite broad and flat so that deviations from Beer's law resulting from the use of relatively heterogeneous radiant energy will be negligible. Sometimes it will not be possible or desirable to work at the point of maximum absorption (Note 5). Where there is interference from other absorbing substances in the solution or where the absorption maximum is sharp, it is sometimes possible to find another flat portion of the curve where the measurements will be free from interference. When no flat portion free from interference can be found, it may be necessary to work on a steep portion of the curve. In this case Beer's law will not hold unless the isolated spectral band is quite narrow. It is not objectionable to utilize a steep part of an absorption curve, provided a typical calibration curve is obtained, except for most instruments the reproducibility of the absorbance readings will be poor unless a fixed wavelength setting of the monochromator is maintained or filters are used. A small change in any of a large number of conditions will decrease the accuracy by a larger amount than when observations are made where the change in absorption is more gradual.