Designation: E 60 – 98

Standard Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry[1]

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 Spectroscopy[3]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[3]

E 169 Practices for General Techniques of Ultraviolet-Visible Quantitative Analysis[3]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[3]

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 section on scope) shall constitute due notification that the photometers, spectrophotometers, and photometric practice

[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.

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

[5] *Annual Book of ASTM Standards*, Vol 03.05.

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 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 (mμ).

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 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, 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 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 nearly 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 In order for a photocell to be useful, it must exhibit a constancy of current with time of exposure. Most commercial alkali cells in use at the present time produce a constant current after an exposure of a few minutes. The photovoltaic cells, on the other hand, 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. Actually, however, this error is usually small and, moreover, many instruments provide individual calibration of the galvanometer.

12.2 Where photoemission cells are used, current amplification is usually resorted to 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 E 168 and E 169). 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 decide upon the spectral region to be used 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. In the ideal case (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 6). In those cases 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. There is no real objection to operation on a steep part of an absorption curve, provided the usual standard calibration curve is obtained, except that with most instruments the reproducibility of the absorbance readings will be poor unless a fixed wavelength setting of the monochromator is maintained or unless 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.

NOTE 6—For example, in some determinations it is convenient to adjust the absorption to the optimum point by varying the wavelength setting of the monochromator rather than by varying the size of the sample.

13.3 In most photometric work it is best to prepare a calibration curve or chart rather than to rely on the assumption of linearity, since it is not at all uncommon to obtain curved lines in the calibration of solutions that are known to obey

Beer's law. The two most common causes of this are the presence of stray radiant energy, and the use of filters or monochromators that isolate too broad a spectral region for the analysis. Nonlinearity will generally be more pronounced the greater the heterogeneity of the radiant energy employed. Thus, one is more likely to obtain linearity with a spectrophotometer having a prism or grating with a high resolving power than with one employing rather broad-banded filters. On the other hand, high resolving power or a narrow slit width is no guarantee of linearity unless stray radiant energy is rigorously excluded. When nonlinearity is encountered at one wavelength setting, it is sometimes possible to eliminate it by changing to another wavelength (where stray radiant energy is negligible) even though the latter is less favorable from the standpoint of flatness and sensitivity. A filter instrument employing a good filter will sometimes yield a more nearly straight calibration curve than can be obtained with certain spectrophotometers. This is especially true in the violet and near ultraviolet regions where stray radiant energy is likely to be encountered in grating monochromators.

13.4 A brief description of the principle of the method will be found in each ASTM test method.

14. Concentration Range

14.1 The concentration of the species being determined should be adjusted preferably so that the transmittance readings fall within the range that yields the minimum error for the amount of constituent being determined. There are several sources of error in photometric analysis, including instrumental and sample manipulative errors, which must be considered when selecting the optimum transmission region. These sources of error have been discussed in detail by Crouch and co-workers **(4).** These workers suggest that the optimum absorbance range for a photometric analysis be determined by preparing a working curve with enough measurements to get standard deviations on each absorbance value. However, for practical purposes, a simple test using a Ringbom-type plot may be useful. The Ringbom method has been discussed by Ayres **(5)** and extended by Carlson.[6]

14.2 The Ringbom test for optimum concentration range for minimum photometric error involves the plotting of experimental calibration data. A plot of the appropriate Ringbom parameter versus logarithm of concentration should exhibit a point of inflection where the relative error in concentration will be a minimum. If this curve is fairly straight over an interval surrounding the point of inflection, all values corresponding to that interval will be approximately as good as the best. The appropriate Ringbom parameter to be used will depend on the relationship between the error in transmittance measurement and transmittance for the specific instrument employed in the analysis. Three such relationships proposed for spectrophotometric instruments **(6)** are tabulated in Table 1. The corresponding Ringbom parameter to be plotted against logarithm of concentration is also given. The parameter to be used depends on the dominant error characteristic of the specific instrument involved in the analysis. The extended Ringbom method cannot determine this error characteristic; it does, however, provide a simple test for determining the optimum analytical range for any assumed dependence of transmittance error on transmittance.

TABLE 1 Relationship Between Error in Transmittance (ET) and Transmittance (T)

Error Relationship	Type of Error	Ringbom Parameter (T = Transmittance)
E_T independent of T	scale reading errors, dark current drift (noise-limited instruments with photovoltaic or thermocouple detectors)	T
$E_T \propto T^{1/2}$	detector shot noise error (photoemissive detectors)	$T^{1/2}$
$E_T \propto T$	cell and sample preparation errors, wavelength error, source change errors	log T

14.3 If the dominant error source for an instrument is not known, the following guidelines are suggested. For any noise-limited instrument with a photovoltaic or thermal detector, error in intensity is independent of intensity and the appropriate Ringbom parameter is transmittance, or absorptance (1-T), as in the original Ringbom method. The optimum transmittance for this case will typically be in the 20 to 60 % range. For modern instruments employing photomultiplier detectors and advanced read-out systems and operating under noise-limited conditions, the $T^{1/2}$ parameter should be applicable. In this case the optimum transmittance is typically found to be in the 5 to 40 % range. The log T parameter may be appropriate for some specific instrument or sample systems, or both, but its use cannot be generalized. The effect of plotting log T is to move the optimum range to even lower transmission.

15. Stability of Absorption

15.1 The absorbing compounds on which photometric methods are based vary greatly in stability. In some instances, the absorption is stable indefinitely, but in the majority of methods the absorption either increases or decreases on standing. In some cases a completely (or relatively) stable absorption is obtained on standing; in other cases it is stable for a time and then changes; in still other cases it never reaches a stable intensity. In all photometric work it is desirable to measure both standards and samples during the time interval of maximum stability of the absorption, provided that this occurs reasonably soon after development of the absorption. In those cases where the absorption changes continuously, it is necessary to control rigidly the time of standing. A statement on the stability of absorption will be found in each ASTM test method.

16. Interfering Elements

16.1 In photometry there are two basic types of methods to be considered: one type in which the photometric measurement is made without previous separations, and a second type in which the element to be determined is partially or completely isolated from the other elements in the sample.

16.1.1 In the first type of method it usually happens that one or more of the elements or reagents present may cause

[6] Supporting data are available from ASTM Headquarters. Request RR: E03 – 1020.

interference with an absorbing reaction. Such interference may be due to the presence of a colored substance, to a suppressive or enhancing effect on the absorption of the substance being measured, or to the destruction or formation of a complex with the reagents thus preventing formation of the absorbing substance. The most important methods, not involving separations, used to eliminate such interferences are as follows:

16.1.1.1 The use of standards whose composition matches the sample being analyzed as closely as possible.

16.1.1.2 Performing the measurement at a wavelength where interference is at a minimum, and

16.1.1.3 The use of reagents that form complexes with the interfering elements.

16.1.1.4 The question as to how much interference can be tolerated in a given method will depend upon many factors, including the degree of accuracy required in the determination. In general it is desirable to avoid using a method where the error to be "blanked out" is appreciable. The methods involving no separations suffer from the distinct disadvantage that the analyst must often know the matrix of the sample to be analyzed and, what is more important, must be able to prepare a standard to duplicate it. This is not always easy to do, for it often happens, especially in the determination of traces, that the so-called pure metals used for preparing the synthetic standards contain more of the element to be measured than does the sample being analyzed.

16.1.2 In the second type of method, the separations may involve removal of one or more interfering elements or may provide for complete isolation of the element in question before its photometric estimation. In this type of method there is usually no attempt made to adjust the matrix of the standard solution to fit that of the sample being analyzed, since presumably all extraneous interference has been removed. The standard in this case is a standard solution of the element in question. In any photometric determination it is desirable to keep the manipulation and separations as simple as possible, for the greater the number of reagents and the more manipulation involved the greater the blank and hence the more chance of error. Very useful tabulations have been compiled of methods used to eliminate interference in photometric analysis **(7,2).**

16.2 A discussion of interfering elements will be found in each ASTM test method.

17. Concentrations of Standard Solutions

17.1 The concentrations of standard solutions shall be expressed in milligrams or micrograms of the element per millilitre of solution.

18. Cell Corrections

18.1 To correct for differences in cell paths in photometric measurements using instruments provided with multiple absorption cells, cell corrections should be determined according to the following procedure: Transfer suitable portions of the reference solution prepared in a specific method to two absorption cells (reference and "test") of approximately identical light paths. Using the reference cell, adjust the photometer to the initial setting using a light band centered at the appropriate wavelength. While maintaining this adjustment, take the absorbance reading of the "test" cell and record as the cell correction. Make certain that a positive absorbance reading is obtained. If it is negative, reverse the positions of the cells. ("Matched" cells frequently show no reading.) Subtract this cell correction (as absorbance) from each absorbance value obtained in the specific method. Keep the cells in the same relative positions for all photometric measurements to which the cell correction applies.

19. Calibration Curve or Chart

19.1 Linear relation between transmittance or absorbance and concentration is not always obtained with commercially available instruments, even though the absorbing system is known to obey Beer's law. Because of this, it is evident that the use of calibration curves or charts will be necessary with such instruments. Moreover, it is not safe, with most instruments on the market today, to use calibration curves or charts interchangeably, even though the photometers may be of the same make and model. A separate calibration curve or chart must be prepared for each instrument.

19.2 The use of a calibration curve or chart in photometric analysis ensures correct measurement of concentration only when the composition of the radiant energy used in the work does not change. In most cases it is necessary to restandardize from time to time to guard against change in the photocell (or photosensitive tube), filters (or monochrometer), measuring circuit, and illuminant.

19.3 When a calibration curve is used, the usual procedure is to plot the values of A, obtained from a series of standard solutions whose concentrations adequately cover the range of the subsequent determinations, against the respective concentrations, on ordinary graph paper. When the scale being used does not read directly in absorbance, it is then convenient to plot concentration, c, against percentage transmittance on semilogarithmic paper, using the semilogarithmic scale for the percentage T values. In some cases it is more convenient to prepare a chart of c *versus* A or percentage T values. In plotting, a straight line should be obtained if a good instrument is employed and if the solution obeys Beer's law. If all blanks and interference have been eliminated, the lines should pass through the origin (the point of zero concentration and zero absorbance or 100 % transmittance). The use of A in the plotting is advantageous because it is directly proportional to the concentration. On the other hand, while percentage transmittance has the disadvantage of decreasing in magnitude as the concentration increases, it is more convenient to use when the instrument employed does not have a scale calibrated in absorbance.

19.4 Detailed instructions for the preparation of calibration curves or charts will be found in each of the ASTM test methods.

20. Procedure

20.1 Detailed instructions for the procedure to be followed will be found in each of the ASTM test methods.

21. Blanks

21.1 In taking the photometric reading of the absorption in any solution, all the components present that absorb radiant

energy in the region of interest must be taken into account. These sources of absorption are:

21.1.1 Absorption of the element sought,

21.1.2 Absorption of the element sought, present as an impurity in the reagents used,

21.1.3 Background,

21.1.4 Absorption of all reagents used,

21.1.5 Absorption produced by reaction of reagents with other elements present, and

21.1.6 Turbidities.

21.1.7 These absorptions are additive and all or some will be included in the photometric reading, depending upon the method of preparing the calibration curve and the reference solution. Items 21.1.5 and 21.1.6 are interferences and are assumed to be eliminated by preliminary conditioning operations. Items 21.1.2 to 21.1.4 have been loosely designated as "blanks." It is less confusing to restrict the usage of the word "blank" to reagent blank, 21.1.2 in the above list. Item 21.1.3 as defined in 3.6 and 21.1.4 is usually taken care of by the "reference solution" (3.7).

21.2 Paragraph 21.1 states the general case, and it is desirable that all these factors be considered in the development of a photometric method. However, it is often possible to combine some or all of these factors into the reference solution. Thus, the reference solution may, in some cases, include the reagent blank, the background, and any absorption due to the reagents used. In other cases it may be desirable to measure the reagent blank alone in order that a check may be had on the purity of the reagents. It should be noted, however, that in the case of absorbing systems that do not obey Beer's law, it may be dangerous to use the reagent blank for the reference solution, particularly if the magnitude of the absorption due to the reagent blank becomes appreciable. In such instances it is necessary to refer both reagent blank and sample solution to some arbitrary reference solution, usually water, and make suitable corrections for the absorption of the reagent blank.

21.3 The requirements for the preparation and measurement or application of these various corrections, both in the preparation of the calibration curve and in the procedure, will be found in each of the ASTM test methods.

22. Precision and Bias

22.1 The primary advantages of photometric and spectrophotometric methods are those of speed, convenience, and relatively high precision and accuracy in the determination of micro- and semimicro-quantities of constituents. For the determination of macro-quantities, differential photometric techniques **(8)** or other analytical techniques are often preferable, since they are generally more accurate when larger quantities are involved. It should be remembered that even under the most favorable circumstances it is difficult to obtain an accuracy better than about 1 % of the amount present in most photometric determinations. This does not mean that it is not practical to analyze macro-samples photometrically. With the continued improvement in optical instruments, it has been possible to perform an increasing number of different types of determinations, especially in the cases where high accuracy is not required. In evaluating the precision and bias of any photometric or spectrophotometric method, the quality of the apparatus and the chemical procedure involved must be considered.

23. Keywords

23.1 photometry; spectrophotometry—absorption

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