Designation: E 1026 – 04$^{\epsilon 1}$

An American National Standard

Standard Practice for
Using the Fricke Reference-Standard Dosimetry System[1]

This standard is issued under the fixed designation E 1026; 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.

ϵ^1 NOTE—Equations 3 and 4 were corrected editorially in August 2005.

1. Scope

1.1 This practice covers the procedures for preparation, testing and using the acidic aqueous ferrous ammonium sulfate solution dosimetry system to measure absorbed dose to water when exposed to ionizing radiation. The system consists of a dosimeter and appropriate analytical instrumentation. The system will be referred to as the Fricke system. It is classified as a reference-standard dosimetry system (see ISO/ASTM 51261).

1.2 The practice describes the spectrophotometric analysis procedures for the Fricke dosimeter.

1.3 This practice applies only to gamma rays, x-rays (bremsstrahlung), and high-energy electrons.

1.4 This practice applies provided the following are satisfied:

1.4.1 The absorbed dose range shall be from 20 to 400 Gy (**1**).[2]

1.4.2 The absorbed-dose rate does not exceed 10^6 Gy·s^{-1}(**2**).

1.4.3 For radioisotope gamma-ray sources, the initial photon energy is greater than 0.6 MeV. For x-rays (bremsstrahlung), the initial energy of the electrons used to produce the photons is equal to or greater than 2 MeV. For electron beams, the initial electron energy is greater than 8 MeV (see ICRU Reports 34 and 35).

NOTE 1—The lower energy limits given are appropriate for a cylindrical dosimeter ampoule of 12-mm outside diameter. Corrections for dose gradients across an ampoule of that diameter or less are not required.

1.4.4 The irradiation temperature of the dosimeter should be within the range of 10 to 60°C.

1.5 *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]

C 912 Practice for Designing a Process for Cleaning Technical Glasses
D 1193 Specification for Reagent Water
E 170 Terminology Relating to Radiation Measurements and Dosimetry
E 178 Practice for Dealing with Outlying Observations
E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers
E 666 Practice for Calculating Absorbed Dose from Gamma or X-Radiation
E 668 Practice for Application of Thermoluminescence-Dosimetry (TLD) Systems for Determining Absorbed Dose in Radiation-Hardness Testing of Electronic Devices
E 925 Practice for the Periodic Calibration of Narrow Band-Pass Spectrophotometers
E 958 Practice for Measuring Practical Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers

2.2 *ISO/ASTM Standards:*

ISO/ASTM 51205 Method for Using the Ceric-Cerous Sulfate Dosimetry System
ISO/ASTM 51261 Guide for Selection and Calibration of Dosimetry Systems for Radiation Processing
ISO/ASTM 51707 Estimating Uncertainties in Dosimetry for Radiation Processing

2.3 *International Commission on Radiation Units and Measurements (ICRU) Reports:*

ICRU Report 34 The Dosimetry of Pulsed Radiation[4]
ICRU Report 35 Radiation Dosimetry: Electrons with Initial Energies Between 1 and 50 MeV[4]
ICRU Report 60 Fundamental Quantities and Units for Ionizing Radiation[4]
ICRU Report 64 Dosimetry of High-Energy Photon Beams based on Standards of Absorbed Dose to Water[4]

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[1] This practice is under the jurisdiction of ASTM Committee E10 on Nuclear Technology and Applications and is the direct responsibility of Subcommittee E10.01 on Dosimetry for Radiation Processing.

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[2] The boldface numbers that appear in parentheses refer to a list of references at the end of this practice.

[3] For referenced ASTM standards, visit the ASTM webiste, 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.

[4] Available from the International Commission on Radiation Units and Measurements (ICRU), 7910 Woodmont Ave., Suite 800, Bethesda, MD 20814.

2.4 *National Research Council Canada (NRCC):*
PIRS-0815 The IRS Fricke Dosimetry System[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *Fricke Dosimetry System*—consists of a liquid chemical dosimeter (composed of ferrous sulfate or ferrous ammonium sulfate in aqueous sulfuric acid solution), a spectrophotometer (to measure optical absorbance) and its associated reference standards, and procedures for its use.

3.1.1.1 *Discussion*—The Fricke dosimetry system is considered a reference-standard dosimetry system. Sodium chloride is usually added to dosimetric solution to minimize the effects of organic impurities.

3.1.2 *molar linear absorption coefficient* (ϵ_m)—a constant relating the spectrophotometric absorbance (A_λ) of an optically absorbing molecular species at a given wavelength (λ) per unit pathlength (d) to the molar concentration (c) of that species in solution:

$$\epsilon_m = \frac{A_\lambda}{(d \times c)}$$

Unit: m^2mol^{-1}

3.1.3 *net absorbance (ΔA)*—change in measured optical absorbance at a selected wavelength determined as the absolute difference between the pre-irradiation absorbance, A_o, and the post-irradiation absorbance, A as follows: $\Delta A = |A - A_o|$

3.1.4 *radiation chemical yield (G(x))*—the quotient of n (x) by $\bar{\epsilon}$, where n (x) is the mean amount of a specified entity, x, produced, destroyed, or changed by the mean energy, $\bar{\epsilon}$, imparted to the matter.

$$G(x) = \left(\frac{n(x)}{\bar{\epsilon}}\right)$$

Unit: $mol \cdot J^{-1}$

3.2 Definitions of other terms used in this standard that pertain to radiation measurement and dosimetry may be found in Terminology E 170. Definitions in E 170 are compatible with ICRU 60; that document, therefore, may be used as an alternative reference.

4. Significance and Use

4.1 The Fricke dosimetry system provides a reliable means for measurement of absorbed dose to water, based on a process of oxidation of ferrous ions to ferric ions in acidic aqueous solution by ionizing radiation **(3)**. In situations not requiring traceability to national standards, this system can be used for absolute determination of absorbed dose, as the radiation chemical yield of ferric ions is well characterized.

4.1.1 In situations requiring traceability to national standards, response of the Fricke system shall be verified by means of comparison of expected and measured dose values. This verification process requires irradiation of dosimeters in a calibration facility having measurement traceability to nationally or internationally recognized standards.

4.2 The dosimeter is an air-saturated solution of ferrous sulfate or ferrous ammonium sulfate that indicates absorbed dose by an increase in absorbance at a specified wavelength. A temperature-controlled calibrated spectrophotometer is used to measure the absorbance.

4.3 The Fricke dosimeter response is dependent on irradiation temperature and measurement temperature. Thus, corrections may have to be applied to the radiation chemical yield (G) for irradiation temperature and to the molar linear absorption coefficient (ϵ) for measurement temperatures.

4.4 The absorbed dose in materials other than water may be calculated using procedures given in Practices E 666 and E 668, and ISO/ASTM 51261, if the material is irradiated under equivalent conditions.

4.5 There are two factors associated with use of the Fricke system at energies below those specified in 1.4.3:

4.5.1 The radiation chemical yield changes significantly at low photon energies **(4)**, and

4.5.2 For electron energy below 8 MeV, dosimeter response requires correction for dose gradients across the dosimeter with a dimension in the beam direction of 12 mm (see ICRU Report 35).

4.6 The lower energy limits given (refer to 1.4.3) are appropriate for a cylindrical dosimeter ampoule of 12-mm outside diameter. With some difficulty, the Fricke system may be used at lower energies by employing thinner (in the beam direction) dosimeters (see ICRU Report 35). Below the lower limits for energy, there will be significant dose gradients across the ampoule wall. In addition, it is difficult to perform accurate calculations for a cylindrical ampoule.

5. Interferences

5.1 The Fricke dosimetric solution response is extremely sensitive to impurities, particularly organic impurities. Even in trace quantities, impurities can cause a detectable change in the observed response. For high accuracy, organic materials shall not be used for any component in contact with the solution, unless it has been demonstrated that the materials do not affect the dosimeter response.

5.2 Traces of metal ions in the irradiated and unirradiated dosimetric solutions can also affect dosimeter response. Therefore, do not use metal in any component in contact with the solutions.

5.3 If flame sealing the dosimeters, exercise care in filling ampoules to avoid depositing solution in the ampoule neck. Subsequent heating during sealing of the ampoule may cause undesirable chemical change in the dosimetric solution remaining inside the ampoule's neck. For the same reason, exercise care to avoid heating the body of the ampoule during sealing.

5.4 Thermal oxidation (as indicated by an increase in optical absorbance), in the absence of radiation, is a function of ambient temperature. At normal laboratory temperatures (about 20 to 25°C), this effect may be significant if there is a long period of time between solution preparation and photometric measurement. This interference is discussed further in 8.4.

5.5 The dosimetric solution is somewhat sensitive to ultraviolet light and should be kept in the dark for long-term storage. No special precautions are required during routine

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[5] Available from the National Research Council, Ionizing Radiation Standards, Institute for National Measurement Standards, Ottawa, Ontario. K1A 0R6.

handling under normal laboratory lighting conditions, but strong UV sources such as sunlight should be avoided.

6. Apparatus

6.1 For the analysis of the dosimetric solution, use a high-precision spectrophotometer capable of measuring absorbance values up to 2 with an uncertainty of no more than ±1 % in the region of 300 nm. Use a quartz cuvette with 5- or 10-mm pathlength for spectrophotometric measurement of the solution. The cuvette capacity must be small enough to allow it to be thoroughly rinsed by the dosimeter solution and still leave an adequate amount of that solution to fill the cuvette to the appropriate level for the absorbance measurement. For dosimeter ampoules of less than 2 mL, this may require the use of semi-microcapacity cuvettes. Other solution handling techniques, such as the use of micro-capacity flow cells, may be employed provided precautions are taken to avoid cross-contamination. Control the temperature of the dosimetric solution during measurement at 25 ± 0.5°C. If this is not possible, determine the solution temperature during the spectrophotometric analysis and correct the results using Eq 4 in 10.4.5.

6.2 Use borosilicate glass or equivalent chemically-resistant glass to store the reagents and the prepared dosimetric solution. Clean all apparatus thoroughly before use (see Practice C 912).

6.2.1 Store the cleaned glassware in a clean, dust-free environment. For extreme accuracy, bake the glassware in vacuum at 550°C for at least one hour (**5**).

6.2.2 As an alternative method to baking the glassware, the dosimeter containers (for example, ampoules) may be filled with the dosimetric solution and irradiated to a dose of at least 500 Gy. When a container is needed, pour out the irradiated solution, rinse the container at least three times with unirradiated solution and then refill with the dosimetric solution to be irradiated. The time between filling, irradiation and measurement should be as short as practical, preferably no more than a few hours. Refer to Note 2.

6.3 Use a sealed glass ampoule or other appropriate glass container to hold the dosimetric solution during irradiation.

NOTE 2—To minimize errors due to differences in radiation absorption properties between the container material and the Fricke solution, it is possible to use plastic containers (for example, PMMA or polystyrene) to hold Fricke solution. However, the interferences discussed in Section 5 may result in a reduction in accuracy. To reduce these problems, the plastic containers may be conditioned by irradiating them filled with dosimetric solution to approximately 500 Gy. The containers should then be thoroughly rinsed with unirradiated solution before use.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the measurements. Methods of obtaining higher purity of chemicals exist (for example, crystallization or distillation), but are not discussed here

7.2 *Purity of Water*—Water purity is very important since water is the major constituent of the dosimetric solution, and therefore, may be the prime source of contamination. The use of double-distilled water from coupled all-glass and silica stills is recommended. Alternatively, water from a high-quality commercial purification unit capable of achieving Total Oxidizable Carbon (T.O.C.) content below 5 ppb may be used. Use of deionized water is not recommended.

NOTE 3—Double-distilled water distilled from an alkaline permanganate ($KMnO_4$) solution (2 g $KMnO_4$ plus 5 g sodium hydroxide (NaOH) in 2 dm^3 of distilled water) has been found to be adequate for routine preparation of the dosimetric solution. High purity water is commercially available from some suppliers. Water labelled HPLC (high pressure liquid chromatography) grade is usually sufficiently free of organic impurities to be used in this practice.

7.3 *Reagents*:

7.3.1 *Ferrous Ammonium Sulfate*—$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$.

7.3.2 *Sodium Chloride* (NaCl).

7.3.3 *Sulfuric Acid* (H_2SO_4).

8. Preparation of Dosimeters

8.1 Prepare dosimetric solution:

8.1.1 Dissolve 0.392 g of ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, and 0.058 g of sodium chloride, NaCl, in 12.5 mL of 0.4 $mol \cdot L^{-1}$ sulfuric acid, H_2SO_4. Dilute to 1 L in a volumetric flask with air-saturated 0.4 $mol \cdot L^{-1}$ sulfuric acid at 25°C. To make 0.4 M solution, use 41.0 g of 96.7 % sulfuric acid plus water to make 1 L of solution.

NOTE 4—Sodium chloride is used to reduce any adverse effects on the response of the dosimeter due to trace organic impurities.

8.1.2 If the final solution is not yet air-saturated, it should be done. Shaking of the solution is normally sufficient to achieve this. Alternatively, bubble high-purity air through the solution, taking care to avoid any possible organic contamination of the air. The oxygen concentration in air-saturated solution is adequate to ensure the dosimeter's linear response up to 400 Gy. Store the dosimetric solution in clean borosilicate glass containers in the dark.

8.2 The dosimetric solution has the following concentrations: 1×10^{-3} mol·L-1 ferrous ammonium sulfate; 1×10^{-3} $mol \cdot L^{-1}$ sodium chloride; and 0.4 $mol \cdot L^{-1}$ sulfuric acid.

8.3 The dosimetric solution will slowly oxidize at room temperature resulting in an increase in the absorbance of the

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[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

unirradiated solution. If the solution has not been used for some time, measure the absorbance of the unirradiated solution, as described in 10.3. If the absorbance of a 10-mm pathlength sample is greater than 0.1, do not use that solution. Prepare a fresh batch of solution to replace it.

NOTE 5—Oxidation of the solution at room temperature can be significantly reduced by refrigerating the solution, but refrigeration may also change the oxygen concentration.

8.4 Rinse the dosimeter containers (ampoules or other types) at least three times with the dosimetric solution before filling them for irradiation. Even with careful rinsing, there will always be solution remaining; subsequent rinsing will help mitigate this effect.

8.5 Fill clean containers with the dosimetric solution. If flame sealing the dosimeters, observe the precautions in 5.3. Separate five dosimeters from the remainder of the batch and do not irradiate them. Use them in determining A_o (see 10.3).

8.6 The quantity of dosimetric solution produced by the procedure in 8.1 is convenient when dosimeters are needed in small quantities. If more dosimeters are required on a regular basis, then it may be more convenient to prepare a concentrated stock solution from which a small quantity may be drawn and diluted as needed (see Appendix X1 for details).

9. Calibration of the Dosimetry System

9.1 The quality of the Fricke dosimetry system is extremely high and it is capable of absolute dose determination using published $\epsilon \cdot G$ value. However, for applications requiring traceability to national standards, the dosimetry system (consisting of a specific batch of dosimeters and specific spectrophotometer) shall be calibrated prior to use, in accordance with the user's documented procedure that specifies details of the calibration process and quality assurance requirements. This calibration process shall be repeated at regular intervals to ensure that the accuracy of the absorbed dose measurement is maintained within required limits. Calibration methods are described in ISO/ASTM 51261.

9.2 An alternative to the methods of calibration described in ISO?ASTM 51261 is to perform the following steps.

9.2.1 Using Fricke dosimeters, remaeasure the absorbed-dose rate in a calibration facility whose dose rate is already known and is traceable to national standards. The observed difference and its uncertainty shall be incorporated in the uncertainty estimates of the Fricke dosimetry system.

9.3 *Calibration Irradiation of Dosimeters*—Irradiation is a critical component of the calibration of the dosimetry system. Calibration irradiations shall be performed at an accredited calibration laboratory, or at an in-house calibration facility meeting the requirements in ISO/ASTM Practice 51400, that provides an absorbed dose (or absorbed-dose rate) having measurement traceability to nationally or internationally recognized standards.

9.3.1 When the Fricke dosimeter is used as a routine dosimeter, the calibration irradiation may be performed per 9.3, or at a production or research irradiation facility together with reference- or transfer-standard dosimeters that have measurement traceability to nationally or internationally recognized standards.

9.4 *Measurement Instrument Calibration and Performance Verification*—For the calibration of the instruments, and for the verification of instrument performance between calibrations, see ISO/ASTM Guide 51261 and instrument-specific operating manuals.

9.4.1 Check the wavelength scale of the spectrophotometer. The emission spectrum from a low-pressure mercury arc lamp can be used for this purpose. Such a lamp may be obtained from the spectrophotometer manufacturer or other scientific laboratory instrument suppliers. Other appropriate wavelength standards are holmium oxide filters or solutions. For more details, see Practices E 275, E 925, and E 958.

NOTE 6—For example, holmium oxide solutions in sealed cuvettes for use in the wavelength region of 240 to 650 nm are available as certified wavelength standards (SRM 2034).[7]

9.4.2 Check the accuracy of the photometric (absorbance) scale of the spectrophotometer, especially in the ultraviolet region before and after each set of measurements. Certified absorbance standard filters or solutions are available for this purpose.

NOTE 7—Solutions such as SRM 931f and SRM 935 (**6**) and metal-on-quartz filters such as SRM 2031[7] are examples of absorbance standards. Note that SRM 935 is a pure chemical that must be diluted by the user.

10. Irradiation and Measurement Procedures

10.1 Irradiations are performed for individual dosimeters or groups of dosimeters for the purpose of absorbed-dose rate determination.

10.2 *Irradiation*:

10.2.1 Specify the dose in terms of absorbed dose to water.

10.2.2 Position the dosimeters in the radiation field in a defined, reproducible location. To avoid creating an air gap between the solution and ampoule wall, the dosimeter should be in the vertical position.

10.2.3 When using a photon source (gamma-rays or X-rays) for irradiation, surround the dosimeters with a sufficient amount of water-equivalent material to achieve approximate electron equilibrium conditions, for example, polystyrene or polyethylene. The appropriate thickness of such material depends on the energy of the photon radiation (see Practices E 666 and E 668).

NOTE 8—For example, for a ^{60}Co source, 3 to 5 mm of polystyrene (or equivalent polymeric material) should surround the dosimeter in all directions.

10.2.4 When using an electron beam for irradiation, locate the dosimeters in a well-characterized position within the radiation field.

10.2.5 Ensure that the radiation field within the volume occupied by the dosimeters is as uniform as possible. The variation in dose rate within this volume should be known, and be within acceptable limits.

10.2.6 Control the temperature of the dosimeters during irradiation, or monitor the temperature variations. This information is needed for response correction (see 10.4).

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[7] Available from the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899.

10.2.7 The required number of sets of dosimeters depends on the absorbed-dose range of utilization. Use a set of at least three dosimeters for each absorbed-dose value, and a minimum of five sets of dosimeters for each factor of ten span of absorbed dose.

NOTE 9—To determine mathematically the minimum number of sets to be used, divide the maximum dose in the range of utilization (*Dmax*) by the minimum dose (*Dmin*), then, calculate log (base 10) of this ratio: $Q = \log(Dmax / Dmin)$. If Q is equal to or greater than 1, calculate the product of $5 \times Q$, and round this up to the nearest integer value. This value represents the minimum number of sets to be used.

10.3 *Measurement*:

10.3.1 Set the spectral bandwidth of the spectrophotometer at no more than 2 nm, and maintain the sample compartment and dosimetric solution at 25 ± 0.5°C during the measurement. Determine the optimum wavelength of the absorbance peak of the solution by making a spectral scan of an irradiated sample. The optimum wavelength is the wavelength that corresponds to the maximum absorption value. The nominal peak wavelength is from 302 to 305 nm. This absorption peak is fairly broad, and the optimum wavelength will vary depending on the quality of the spectrophotometer. Set the wavelength at the peak and leave it there for subsequent measurements.

10.3.2 Set the balance of the spectrophotometer to zero with only air (no cuvette) in the light path(s).

10.3.3 Fill a clean cuvette (or flow cell) of 5 or 10 mm pathlength with distilled water. Carefully clean the cuvette exterior windows through which the light beam passes. Measure and record the absorbance. See Note 10.

10.3.4 Empty the water from the cuvette (or flow cell) and rinse it at least twice with the solution from an ampoule, or other container. Discard the rinse solution and fill to the appropriate level with more solution from the same container. Carefully wipe off any solution on the exterior surfaces of the cuvette. Place the cuvette in the sample holder of the spectrophotometer and measure the absorbance as soon as the instrument reading has stabilized. It is important to read the absorbance of each dosimeter at the same elapsed time after putting it in the spectrophotometer light beam. This is necessary because the absorbance increases slowly with time while the dosimeter is in the light beam (probably due to oxidation of the solution by the UV light). Repeat this procedure for all unirradiated and irradiated solutions.

NOTE 10—Inadequate rinsing of the cuvette (or flow cell) between dosimeter solutions can lead to errors due to solution carryover (cross-contamination). Techniques for minimizing this effect are discussed in Ref (**6**). Micropipettes or Hamilton dispensers are recommended for the rinsing procedure. It is not meaningful to attempt to determine the quality of the water from absorbance measurements of water since pure water has an absorbance of approximately 0.0002 at 303 nm. The loss of light due to reflection from the cuvette surfaces will increase the absorbance.

10.3.5 Periodically, check the spectrophotometer zero after each measurement using only air in the light path(s). Read the unirradiated solution before and after the irradiated solutions are read. . Periodically during the measurement process, remeasure the absorbance of a distilled water to detect any contamination of the cuvette (or flow cell) and take appropriate corrective actions if required.

10.4 *Analysis*:

10.4.1 For the absorption peak, calculate the mean absorbance of the unirradiated dosimeters, A_o (see 8.6). From the absorbance of the irradiated dosimeter (A), calculate the net absorbance, ΔA, for each irradiated dosimeter as follows:

$$\Delta A = |A - A_o| \quad (1)$$

10.4.2 The basic equation for calculation of absorbed dose in the dosimeter solution, D_F, is as follows:

$$D_F = \frac{\Delta A}{\epsilon \cdot G \cdot \rho \cdot d} \quad (2)$$

where:

D_F = absorbed dose to the Fricke solution (Gy),
ΔA = net absorbance at the optimum wavelength (302 to 305 nm),
ρ = density of the dosimetric solution, equal to 1.024×10^3 kg·m^{-3},
ϵ = molar linear absorption coefficient of the ferric ions (Fe^{3+}), m^2·mol^{-1},
G = radiation chemical yield of ferric ions (Fe^{3+}), mol·J^{-1}, and
d = optical pathlength of the dosimetric solution in the cuvette, m.

10.4.3 When using Eq 2, the values of the parameters on the right hand side of the equation must be those for the appropriate temperatures, that is, the value of ϵ must be its value for the temperature at which the absorbance of the Fricke solution was measured and the value of G must be its value for the temperature at which the Fricke solution was irradiated. The values of ϵ and G are well known for 25°C and their temperature coefficients are known. The values of ϵ, G, or the product $\epsilon \cdot G$ for a given temperature can be calculated using Eq 3 and 4 (see NRCC Report PIRS-0815). Both $\epsilon(Fe^{3+})$ and $G\ (Fe^{3+})$ increase with increase in temperature.

$$\epsilon_{T_{read}} = \epsilon_{25}[1 + 0.0069\ (T_{read} - 25)] \quad (3)$$

$$G_{T_{irrad}} = G_{25}[1 + 0.0012\ (T_{irrad} - 25)] \quad (4)$$

NOTE 11—Although ICRU 35 is an important reference, equation (5.7) within ICRU 35 gives the temperatures in the brackets in the reverse order to the correct order. ICRU 64 gives the equation in the correct form, but it references ICRU 35 with no mention of the error.

10.4.4 The values of ρ and d should also correspond to their values at the temperature of the Fricke solution when the absorbance was measured. The use of "room temperature" values is usually considered adequate for precise dosimetry. Eq 3 and 4 are valid for an irradiation temperature range of 10 to 60°C, and for an absorbance measurement temperature range of 15 to 35°C.

NOTE 12—Based on Eq 3 and 4, it can be seen that $\epsilon(Fe^{3+})$ and $G\ (Fe^{3+})$ increase with increase in temperature. The recommended values for ϵ and G at 25°C are: $\epsilon = 219$ m^2·mol^{-1} and $G = 1.61 \times 10^{-6}$ mol·J^{-1} (see ICRU Reports 14 and 35). A procedure for determining ϵ is given in Appendix X2.

10.4.5 The values of ϵ and G may have to be corrected for temperature according to Eq 3 and 4. The temperature at which the absorbance of the Fricke solution was measured and the temperature at which it was irradiated must be known.

$$D_F = \frac{\Delta A[1 + 0.0069(25 - T_{read})]\,[1 + 0.0012(25 - T_{irrad})]}{\epsilon_{25}\, G_{25}\, \rho\, d} \quad (5)$$

NOTE 13—In bringing the "correction" from the denominator to the numerator, the temperature subtraction in the round brackets has been reversed. This is not an exact way to achieve the results of Eq 3 and 4, but the errors caused are usually considered negligible. For example, if the absorbance were measured at 30°C, Eq 5 would give a value 0.1 % smaller than Eq 3, and if the irradiation temperature were 60°C, Eq 5 would give a value 0.2 % smaller than Eq 4.

10.4.6 To calculate the absorbed dose to water, D_W, (ICRU Report 35), use the following:

$$D_W = 1.004\ D_F \tag{6}$$

NOTE 14—Eq 6 is valid only for an irradiation temperature of 25°C and a reading temperature of 25°C.

10.4.7 The absorbed dose to water, D_W, can also be determined from the mean absorbed dose in the Fricke solution, D_F, using the following equation (ICRU 64):

$$D_W = (\mu_{en}/\rho)_{W,F}\, p_{W,F}\, D_F \tag{7}$$

where $(\mu_{en}/\rho)_{W,F}$ is the ratio of the mass-energy absorption coefficients of water to Fricke solution; $p_{W,F}$ is the correction factor of the perturbation introduced by the dosimeter vessel if it is not water-equivalent. If a single plastic irradiation cell is used, $p_{W,F}$ is generally negligible.

10.4.8 It has been recommended that the product $\epsilon \cdot G$ be used in (Eq 2 and Eq 5) rather than individually determined ϵ and G values (see ICRU Report 35). This is due to the large systematic errors in the measurement of ϵ that have been observed with a number of investigators. For irradiation and absorbance measurement at 25°C, the recommended value for $\epsilon \cdot G$ at 303 nm is 3.52×10^{-4} $m^2 \cdot J^{-1}$. For irradiation or absorbance measurement at other than 25°C, correct the value of $\epsilon \cdot G$ using Eq 3 and 4.

10.4.9 For an irradiation and absorbance measurement temperature of 25°C, with a 10-mm pathlength cuvette, and using the value of $\epsilon \cdot G$ recommended in 10.4.8, Eq 2 reduces to:

$$D_W = 278\ \Delta A \tag{8}$$

NOTE 15—If the desired outcome is to measure absorbed-dose rate, plot the values of ΔA versus time. Calculate the best straight line fit. The slope of the straight line is the ΔA per unit time. The statistics of the straight line fit indicate the magnitude of the type *A* uncertainties. Due to these uncertainties, the best straight line may, or may not extrapolate to zero absorbance at zero time. The presence of oxidizable impurities in the dosimeter solution may casue the line to shift. Nevertheless, a satisfactory fit of the data to a straight line often indicates that impurities were removed by the radiation. Convert ΔA per unit time into absorbed dose per unit time using Eq 2.

NOTE 16—Impure solutions may exhibit a linear response in terms of ΔA versus dose, but with an enhanced radiation chemical yield (G). A useful method to check the purity of Fricke solution is to compare the dosimetric response (ΔA) of irradiated Fricke solution with and without NaCl (all other aspects of the preparation remaining the same). If the solutions are pure, the difference in response of solutions with and without NaCl should be less than 0.5 %.

11. Minimum Documentation Requirements

11.1 Record calibration data and results (if performed).

11.1.1 Record the dosimeter batch number (code).

11.1.2 Record or reference the date, irradiation temperature, measurement temperature, temperature variation (if any), dose range, radiation source, and associated instrumentation used to calibrate and analyze the dosimeters.

11.2 *Application*:

11.2.1 Record the date and temperature of irradiation, temperature variation (if any), and the date and temperature of absorbance measurement, for each dosimeter.

11.2.2 Record or reference the radiation source type and characteristics.

11.2.3 Record the absorbance, net absorbance value, temperature correction (if applicable), and resulting absorbed dose for each dosimeter. Reference the calibration curve (if appropriate) or the calculations used to obtain the absorbed dose values.

11.2.4 Record or reference the measurement uncertainty in absorbed dose (refer to Section 12).

11.2.5 Record or reference the measurement quality assurance plan used for the dosimetry system application.

12. Measurement Uncertainty

12.1 To be meaningful, a measurement of absorbed dose shall be accompanied by an estimate of uncertainty.

12.2 Components of uncertainty shall be identified as belonging to one of two groups:

12.2.1 *Type A*—Those evaluated by statistical methods, or

12.2.2 *Type B*—Those evaluated by other means.

12.3 Other ways of categorizing uncertainty have been widely used and may be useful for reporting uncertainty. For example, the terms precision and bias or random and systematic (non-random) are used to describe different categories of uncertainty.

12.4 If this practice is followed, the estimate of the expanded uncertainty of an absorbed dose determined by this dosimetry system should be less than 3 % for a coverage factor $k = 2$ (which corresponds approximately to a 95 % level of confidence for normally distributed data), when Fricke is used as an absolute dosimeter. Otherwise, the expanded uncertainty may be higher.

12.5 With great care, lower uncertainties may be achieved (**9**).

NOTE 17—The identification of Type A and Type B uncertainties is based on methodology for estimating uncertainties published in 1993 by the International Organization for Standardization (ISO) in the Guide to the Expression of Uncertainty in Measurement (**9**). The purpose of using this type of characterization is to promote an understanding of how uncertainty statements are arrived at and to provide a basis for the international comparison of measurement results.

NOTE 18—ISO/ASTM 51707 defines possible sources of uncertainty in dosimetry performed in radiation processing facilities, and offers procedures for estimating the magnitude of the resulting uncertainties in the measurement of absorbed dose using a dosimetry system. The document defines and discusses basic concepts of measurement, including estimation of the measured value of a quantity, "true" value, error and uncertainty. Components of uncertainty are discussed and methods are provided for estimating their values. Methods are also provided for calculating the combined standard uncertainty and estimating expanded (overall) uncertainty.

13. Keywords

13.1 absorbed dose; dosimetry; ferrous ammonium sulfate dosimeter; ferrous sulfate dosimeter; Fricke dosimeter; reference-standard dosimeter; transfer-standard dosimeter

APPENDIXES

(Nonmandatory Information)

X1. ALTERNATIVE METHOD FOR PREPARATION OF DOSIMETRIC SOLUTION

X1.1 As an alternative to the preparation of the dosimetric solution described in 8.1, two separate concentrated stock solutions may be prepared and diluted as needed.

X1.2 Prepare concentrated stock solutions as follows:

X1.2.1 Dissolve 19.608 g of ferrous ammonium sulfate in 50 mL of 0.4 mol·L^{-1} sulfuric acid, H_2SO_4, and add 0.4 mol·L^{-1} sulfuric acid to make 100 mL of solution. The resulting concentration is 0.5 mol·L^{-1} ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$.

X1.2.2 Dissolve 2.923 g of sodium chloride in 50 mL of 0.4 mol·L^{-1} sulfuric acid and add 0.4 mol·L^{-1} sulfuric acid to make 100 mL of solution. The resulting concentration is 0.5 mol·L^{-1} sodium chloride, NaCl.

X1.2.3 Store these stock solutions in clean borosilicate glass containers in the dark.

X1.3 Prepare the dosimetric solution from the concentrated solutions as follows:

X1.3.1 Pipette 1 mL of ferrous ammonium sulfate solution and 1 mL of sodium chloride solution from the stock solutions into a 500 mL volumetric flask.

X1.3.2 Add 0.4 mol·L^{-1} sulfuric acid to make 500 mL of solution.

X1.4 The resulting dosimetric solution will have the same molar concentration as that given in 8.2.

X1.5 Prepare the dosimetric solution fresh each time it is needed and store in clean borosilicate glass containers in the dark.

X2. PROCEDURE FOR DETERMINATION OF ϵ FOR FERRIC IONS

X2.1 Even though it is recommended in 10.4 that the product $\epsilon \cdot G$ be used in calculating the dose, there is some merit in determining the value of ϵ experimentally for the particular spectrophotometer utilized in measuring the dosimeter absorbance. In so doing, the performance of the spectrophotometer is independently verified. A series of ferric ion solutions of different concentrations is prepared and measured with the spectrophotometer. The molar linear absorption coefficient is determined from the slope of the line (plot of $\Delta A/d$ versus concentration). The slope should have a value close to 219 m^2·mol^{-1} (see Note 11).

X2.2 Prepare a concentrated ferric ion solution as follows:

X2.2.1 Weigh about 100 mg of spectrographically pure (purity of at least 99.99 %) iron wire to the nearest 0.1 mg.

X2.2.2 Place the iron wire in a long-necked 1000-mL calibrated volumetric flask.

X2.2.3 Add 60 mL of distilled water and 22.5 mL of concentrated sulfuric acid (density of 1.84 g·cm^{-3}).

X2.2.4 Heat the unstoppered flask gently under a hood until the wire is completely dissolved. With a beaker inverted over the mouth of the flask, allow the solution to cool. During these procedures, fix the neck of the flask at an angle of 45° to the horizontal to prevent loss of solution.

X2.2.5 Add 3 to 5 mL of 35 % hydrogen peroxide, H_2O_2, solution to the flask and boil under reflux condensation for ½ to 1 h, or until the bubbles of excess peroxide are driven off. Allow the flask to cool and place it in a thermostat set at 25 ± 0.5°C. H_2O_2 will absorb slightly at 303 nm, so it is imperative that the bubbles have been driven off.

X2.2.6 Dilute the solution with distilled water to give 1000 mL of solution.

X2.3 The molarity (mol·L^{-1}) of ferric ions, C_{ref}, in this reference solution is calculated by the following:

$$C_{ref} = m_{Fe}k/V \qquad (X2.1)$$

where:

m_{Fe} = mass of iron dissolved, kg,
V = volume of the final solution, L, and
k = conversion factor equal to 17.91 mol·kg^{-1} of iron.

X2.4 The reference solution will have an absorbance of about 4 at 303 nm. Pipette samples of the reference solution of 1, 5, 10, 15, 20, and 25 mL into six 100-mL volumetric flasks. Dilute each sample by filling to the 100-mL mark with 0.4 mol·L^{-1} sulfuric acid. These samples should have absorbances ranging from about 0.04 to 1.

X2.5 The molarity of each diluted sample solution, C_s, is calculated by the following:

$$C_s = C_{ref}/S \qquad (X2.2)$$

where:

S = final volume (100 mL) divided by the initial sample volumes (1, 5, 10, 15, 20, and 25 mL).

X2.6 Measure the absorbance of the diluted sample solutions in a 10-mm pathlength cuvette at a temperature of 25 ± 0.5°C using the procedures of 10.3.

X2.7 Plot the absorbance/pathlength values versus concentration of the samples. The result should be a straight line; the slope is the molar linear absorption coefficient. Compare this slope with the reference value of 219 $m^2 \cdot mol^{-1}$.

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