



Designation: E 1026 – 03

Standard Practice for Using the Fricke Reference-Standard Dosimetry System¹

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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:

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.

C 912 Practice for Designing a Process for Cleaning Technical Glasses³

D 1193 Specification for Reagent Water⁴

E 170 Terminology Relating to Radiation Measurements and Dosimetry⁵

E 178 Practice for Dealing with Outlying Observations⁶

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁷

E 666 Practice for Calculating Absorbed Dose from Gamma or X-Radiation⁵

E 668 Practice for Application of Thermoluminescence-Dosimetry (TLD) Systems for Determining Absorbed Dose in Radiation-Hardness Testing of Electronic Devices⁵

E 925 Practice for the Periodic Calibration of Narrow Band-Pass Spectrophotometers⁸

E 958 Practice for Measuring Practical Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers⁹

2.2 ISO/ASTM Standards:

ISO/ASTM 51205 Method for Using the Ceric-Cerous Sulfate Dosimetry System⁵

ISO/ASTM 51261 Guide for Selection and Calibration of Dosimetry Systems for Radiation Processing⁵

ISO/ASTM 51707 Estimating Uncertainties in Dosimetry for Radiation Processing⁵

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

ICRU Report 34 The Dosimetry of Pulsed Radiation¹⁰

ICRU Report 35 Radiation Dosimetry: Electrons with Initial Energies Between 1 and 50 MeV¹⁰

ICRU Report 60 Fundamental Quantities and Units for Ionizing Radiation¹⁰

ICRU Report 64 Dosimetry of High-Energy Photon Beams based on Standards of Absorbed Dose to Water¹⁰

2.4 National Research Council Canada (NRCC):

³ Annual Book of ASTM Standards, Vol 15.02.

⁴ Annual Book of ASTM Standards, Vol 11.01.

⁵ Annual Book of ASTM Standards, Vol 12.02.

⁶ Annual Book of ASTM Standards, Vol 14.02.

⁷ Annual Book of ASTM Standards, Vol 03.05.

⁸ Annual Book of ASTM Standards, Vol 14.01.

⁹ Annual Book of ASTM Standards, Vol 03.06.

¹⁰ Available from the International Commission on Radiation Units and Measurements (ICRU), 7910 Woodmont Ave., Suite 800, Bethesda, MD 20814.

PIRS-0815 The IRS Fricke Dosimetry System¹¹

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: $\text{m}^2\text{mol}^{-1}$

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

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

¹¹ Available from the National Research Council, Ionizing Radiation Standards, Institute for National Measurement Standards, Ottawa, Ontario, K1A 0R6.

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 $\pm 1\%$ 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 $25 \pm 0.5^\circ\text{C}$. 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. 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. The time between filling, irradiation and measurement should be as short as practical, preferably no more than a few hours.

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.¹² Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit

¹² *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.

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 dm³ 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*— $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

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, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 0.058 g of sodium chloride, NaCl, in 12.5 mL of 0.4 mol·L⁻¹ sulfuric acid, H_2SO_4 . Dilute to 1 L in a volumetric flask with air-saturated 0.4 mol·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·L⁻¹ sodium chloride; and 0.4 mol·L⁻¹ sulfuric acid.

8.3 The dosimetric solution will slowly oxidize at room temperature resulting in an increase in the absorbance of the 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 calibration described in 9.1 is to perform a response check of Fricke dosimeters. The response check may be performed by using the Fricke system to determine the dose rate in a calibration facility whose dose rate is already known and is traceable to national standards. The Fricke dosimeter is acceptable for use, if the agreement between the two dose rate determinations is within specified limit (typically 2 %). The limit specified for acceptable agreement shall be incorporated into 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).¹³

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 2031¹³ 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 ⁶⁰Co 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).

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 (D_{max}) by the minimum dose (D_{min}), then, calculate log (base 10) of this ratio: $Q =$

¹³ Available from the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899.