National Institute of Standards & Technology

Certificate

Standard Reference Material 4500
Radiochromic Solution for Reference Dosimetry

This Standard Reference Material (SRM) is intended for the measurement of high absorbed doses of gamma radiation (e.g., from ^{60}Co or ^{137}Cs sources) in the dose range of 50 gray to 5 kilogray (5 to 500 kilorad). SRM 4500 consists of a set of 6 amber glass ampoules each containing 4.5 mL of a radiochromic dye solution. The dye is a 2 mM solution of hexa(hydroxyethyl) pararosaniline cyanide in 85% n-propanol (by volume), 15% dimethyl sulfoxide (by volume), with glacial acetic acid at a concentration of 68 mM, and 500 parts-per-million (by weight) of p-nitrobenzoic acid. The radiochromic dye solution remains colorless when stored in the dark and then becomes irreversibly colored when irradiated due to the formation of a broad absorption band in the visible spectrum. The irradiated solution has a linear response in terms of an increase in spectral absorbance at a wavelength of 600 nm as a function of absorbed dose in water, $D(H_2O)$.

Procedures for using the radiation chemical yield and the molar linear absorption coefficient at 600 nm of these standard solutions to determine absorbed dose are given in the Notes on SRM 4500 (attached). Procedures for measuring the absorbance of the solutions are given in Appendix B.

Caution: This material is light sensitive, especially to ultraviolet light. It is recommended that the material be stored in the dark until used. If properly stored, this SRM is expected to have a shelf life of twelve months from the date of issue.

This SRM was developed and prepared under the direction of W. L. McLaughlin, Project Leader, and M. Farahani. Assistance in determining the properties of the SRM was provided by J. Humphreys, D. Hocken, L. Sheahen and S. Monaco; confirmatory measurements were made by M. Desrosiers and M. Walker.

This Standard Reference Material was prepared in the Center for Radiation Research, Ionizing Radiation Division, Radiation Interactions and Dosimetry Group, Bert M. Coursey, Group Leader.

Gaithersburg, MD 20899
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W.P. Reed, Acting Chief
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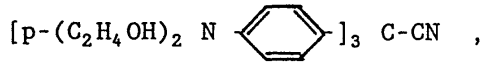
Notes on Standard Reference Material 4500,
Radiochromic Solution for Reference Dosimetry

INTRODUCTION

Radiochromic triphenylmethane leuco dyes are widely used in solid and liquid solutions for the measurement of large absorbed doses of ionizing radiation. The hexa(hydroxyethyl)pararosaniline leuco cyanide (HHEV-CN) dye precursor used as the active solute in this SRM is a white micro-crystalline powder. It has the formula



with a molecular weight of 578.715 g mol^{-1}. The dye solute is added at 2 mM concentration to the mixture of the solvents (15% DMSO and 85% n-propanol by volume), which already contains 68 mM of acetic acid and 500 ppm (by weight) p-nitrobenzoic acid.

The radiation chemical effect involves the cleavage of the cyanide moiety followed by salt isomerization of one of the substituted phenyl groups into a highly absorbing chromophore. This final stable radiolytic product in polar solvents is the carbonium ion of the triphenylmethane dye, hexa(hydroxyethyl) violet, the reverse reaction to leuco dye bases being inhibited by the presence of a weak acid (e.g., acetic acid). The dye product generally has a molar linear absorption coefficient, at wavelengths of the maximum of the dye absorption band, of the order of 10^5 L mol^{-1} cm^{-1}.

DOSIMETRY APPLICATIONS

This well-characterized Standard Reference Material may be used to calibrate gamma-ray sources by irradiating samples to several doses and quantitating the color change by spectrophotometry. At this time SRM 4500 is only certified for gamma-ray dose measurements in the range of 50 gray to

5 kilogray (5 to 500 kilorad).

The basic equation for computing the absorbed dose to water $D(H_2O)$, in units of gray, is given by

$$D(H_2O) = \frac{\Delta A}{\ell \ \rho \ \epsilon_M \ G} \quad ,$$

where ΔA = change in absorbance
ℓ = optical pathlength (cm)
ρ = density (g cm^{-3})
ϵ_M = molar linear absorption coefficient (L mol^{-1} cm^{-1})
and G = chromophore yield (mol J^{-1}).

The molar linear absorption coefficient ϵ_M is reported to be 1.00×10^5 L mol^{-1} cm^{-1} at a wavelength of 600 nm (Rativanich et al., 1981). The G value has been measured using the NIST ^{60}Co pool-type irradiator. This value is 5.05 nmol J^{-1}. The measured density of the solution is 0.845 g cm^{-3}.

This certification is given in terms of absorbed dose to water. There is a relatively small energy dependence relative to biological tissues (e.g., muscle) and water (McLaughlin et al., 1985). For other materials such as silicon electronic devices or polymeric materials, the standard correction factors relative to water should be applied.

More sensitive radiochromic dosimeters can be prepared with higher concentrations of dye (Farahani et al. (1989)). In the future these materials may also be certified for electron beam dosimetry.

FACTORS INFLUENCING THE ACCURACY OF SRM 4500 DOSE MEASUREMENTS

In order to optimize dose calibrations using SRM 4500, several factors need to be considered:

Light Sensitivity

SRM 4500 is very sensitive to light, especially to ultraviolet light. This sensitivity is minimized by the storage of the liquid in amber colored ampoules, which screen out a large portion of the ultraviolet light. Stored in such ampoules, the shelf life is estimated to be at least twelve months from the date issued. It is recommended, however, that the ampoules be stored in the dark until needed, and that during measurement the room light source be covered with a UV-blocking screen or filter, and that the sample be in the spectrophotometer light beam only long enough to make the measurement.

Irradiation Procedure

This SRM may be used in at least two different types of irradiation facilities: (1) a calibration facility that is used to calibrate the response of routine dosimeters and (2) an industrial radiation processing facility that is used to irradiate products such as medical goods or polymers. The irradiation procedures required to use this SRM properly are different for each type of facility.

For a calibration facility the ampoules should be surrounded by appropriate buildup material (e.g., 5 mm of polystyrene for ^{60}Co gamma sources) so as provide approximate electron equilibrium conditions. At least two ampoules should be used for each irradiation. The radiation field should be mapped so that the ampoules can be located in a consistent and reproducible manner in that field.

For a radiation processing facility the ampoules may be placed in or on the product being irradiated. Routine dosimeters may be placed side-by-side with the ampoules as the product is run through the irradiation cycle. The radiation field should be mapped and the ampoules located in a manner so as to avoid any inhomogeneities or sharp dose gradients. A minimum of two ampoules should be used at each location.

Dose Rate Effects on Overall Dose Determination

SRM 4500 has been irradiated with sources having dose rates over the range of 0.4 to 150 gray min^{-1} with less than 1% variation observed in the absorbance value corresponding to the same dose.

Temperature Coefficient During Irradiation

The temperature coefficient during irradiation was found to have a positive slope as shown in Figure 1. Extremes in temperature should therefore be avoided and corrections applied where conditions are significantly different from ambient.

Temperature Coefficient During Spectrophotometric Analysis

The absorbance varies less than 0.1% for a measurement temperature range of 18 to 28°C.

Uncertainties in Dose Determination

If this SRM is properly and carefully employed, the overall uncertainty that can expected in the dose determined is estimated to be 2.6% at a 95% confidence level. Appendix A lists the various sources of uncertainty and their magnitudes, both random and nonrandom, that contribute to the overall uncertainty. Because NIST can not control the end use of this SRM, NIST can not guarantee the results of dose measurements made with it.

ACKNOWLEDGMENT

NIST is indebted to the following individuals and their respective national Laboratories for their confirmatory measurements on some of the properties certified for SRM 4500: Dr. Peter Sharpe, National Physical Laboratory, Teddington, United Kingdom, and Mr. Arne Miller, Risø National Laboratory, Roskilde, Denmark.

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APPENDIX A

Estimated Uncertainties in Absorbed Dose Assessments and Radiation Chemical Yields of Dye Formation for Gamma-Ray Irradiations of Radiochromic Dye Solutions. (Each uncertainty value in percent is equivalent to one standard deviation) (Giacomo, 1981).

	Type A (random)	Type B (other)
gravimetric measurements	0.10	
volumetric measurements	0.10	
determination of ϵ_M for the dye	0.50	1.0
spectrophotometer wavelength		0.01
measurement of ΔA	0.20	
measurement of solution density	0.10	
optical pathlength, ℓ		0.1
irradiation timing	0.23	
radiation field nonuniformity	0.25	
graphite calorimeter measurement		0.2
absorbed dose in water calculated from absorbed dose in graphite		0.3
attenuation correction for electron equilibrium layer and dosimeter ampoule		0.03
source decay correction		0.01
temperature coefficient correction		0.3
summation in quadrature	0.66	1.1
Type A and Type B combined (quadrature)	1.3	
overall uncertainty (2 x combined) (95% C.L.)	2.6	

APPENDIX B

Suggested Protocol for Analysis of SRM 4500

General Comments

The spectrophotometer should be used in accordance with the manufacturer's recommended operating procedures with regard to warm-up time, slit width, scanning speed, etc. Because the absorption peak for this SRM solution is rather broad, measurement of absorbance at the peak is not very sensitive to spectral band pass (slit width). A spectral band pass of 1-3.5 nm should be satisfactory. Once a set of operating parameters is chosen, these parameters should remain constant throughout the measurement process. The windows of the cuvette used to hold the solution during measurement must be kept scrupulously clean at all times and should be checked each time the cuvette is touched. The cuvette should be placed in the analyzing light beam in the spectrophotometer in a consistent and reproducible orientation and position. It should be filled with the dye solution to an appropriate and consistent level each time. The instrument should be checked periodically during the measurement session to assure that no drifting of zero balance, spectral band pass, wavelength, or any other parameter occurs. Specific procedures for performing the measurements are as follows:

1. Turn on the spectrophotometer and allow it to warm up and completely stabilize before making any measurements.

2. For spectrophotometers with automatic baseline correction, record the baseline with air only (no cuvette or solution) in the light path(s) over the wavelength range of 700 to 325 nm. After recording, check the baseline by running a scan; it should be a straight line within the limits of the instrument's baseline correction specifications. Set the wavelength at 700 nm and the balance (zero) of the absorbance scale at zero.

3. Use a high-quality, clean cuvette with a 10-mm pathlength. Rinse both the inside and outside of the cuvette thoroughly with double-distilled water,

then with pure methanol, and air dry. High-purity compressed air may be used for drying to expedite the measurement process.

4. Transfer a small fraction of the solution from an unirradiated SRM ampoule into the cuvette by means of a transfer syringe or pipette. Rinse the cuvette with this solution then discard the solution.

5. Transfer the remainder of the unirradiated solution into the cuvette. Clean the outside windows of the cuvette with methanol and wipe dry with clean tissue. Place the cuvette in the sample light beam of the spectrophotometer.

6. Check the absorbance of the solution at the nominal peak of 600 nm and set the absorbance range accordingly so that the recording will remain on scale.

7. Reset the wavelength to 700 nm and run a spectrum scan until the recording goes off scale at the high absorbance limit, usually at a wavelength of about 375 nm. Record the absorbance value, A_0, at the peak of the spectrum, the peak normally occurring very close to 600 nm.

8. Remove the cuvette, transfer the solution back into its ampoule for later use, rinse the cuvette and the transfer syringe (or pipette) thoroughly with methanol, and air dry.

9. Repeat steps 4. and 5. with a second unirradiated ampoule. Record the absorbance value, A_0, of that solution at the peak of the spectrum. Take the average of the two A_0 values measured as the final A_0 to be used in the calculation of ΔA. Repeat step 8.

10. Set the spectrophotometer back to 700 nm and recheck the zero balance with air only in the light path(s).

11. Fill the cuvette with solution from an irradiated ampoule, and follow the procedures of 4. through 10. above. Record the peak absorbance value,

A_i, at 600 nm. It is not necessary to run a spectral scan on every solution once the wavelength position of the peak has been accurately determined.

11. Calculate $\Delta A = A_i - A_0$ for each irradiated ampoule.

12. Periodically during the measurement process (for example, after each set of irradiated ampoules is analyzed), check the value of the unirradiated solution, A_0. Any drift in this value may be indicative of contamination of the cuvette. Take appropriate corrective action if required.

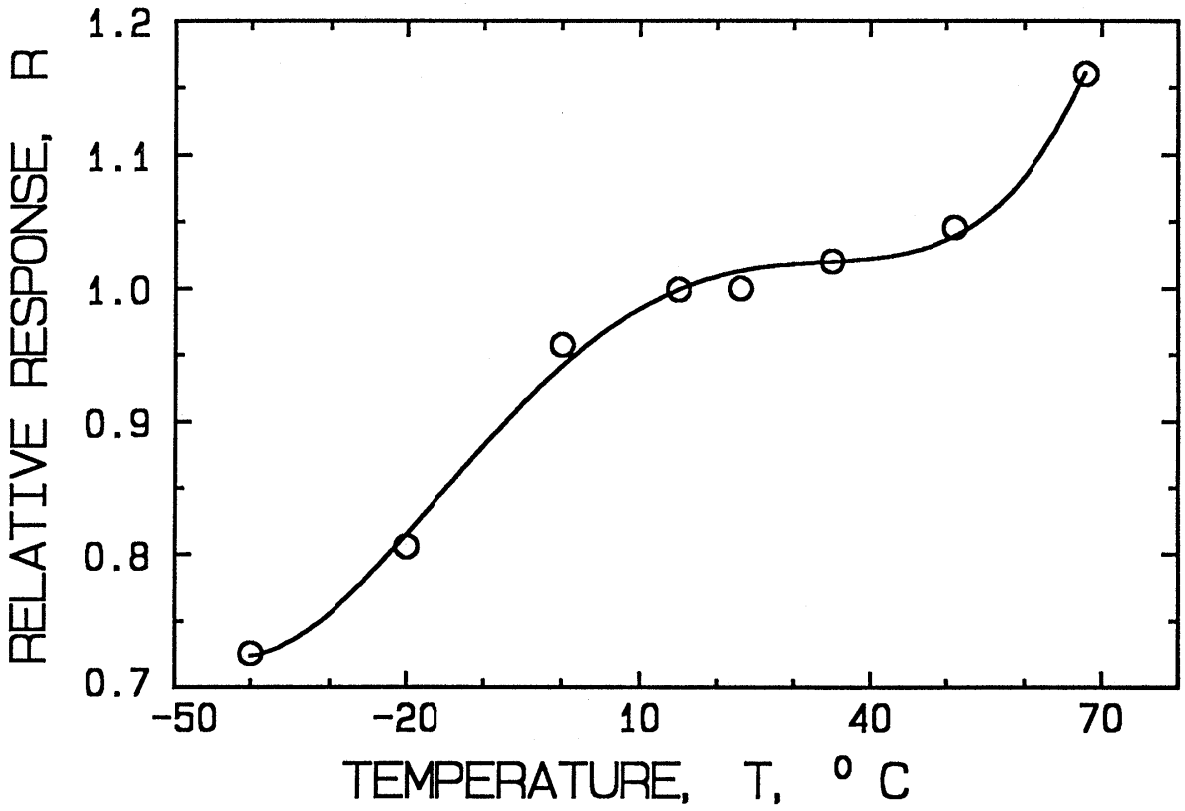

Fig. 1. Temperature dependence of SRM4500

Fitted curve: $R = 0.9415 + 5.212\times10^{-3}\ T - 8.363\times10^{-5}\ T^2 - 9.250\times10^{-7}\ T^3 + 2.544\times10^{-8}\ T^4$