National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1935a

Potassium Dichromate Solution
for Use as an Ultraviolet Absorbance Standard

This Standard Reference Material (SRM) is intended for use as a reference standard for verifying the accuracy of the absorbance scale of absorption spectrometers that can provide an effective bandpass of 2 nm or less at 235 nm, 257 nm, 313 nm, and 350 nm. Such verification is accomplished by comparing the measured apparent absorbances, A(meas), to the certified apparent absorbances, A(cert), as described under the "Instructions for Use" section of this certificate. The term "apparent absorbances" is used because no corrections have been applied to the absorbance data for the effects of internal multiple reflections within the cuvette. These corrections do not exceed 0.2 %. The nomenclature used in this certificate is that recommended by K.D. Mielenz [1].

A unit of SRM 1935a contains five blank solutions and five sample solutions, for a total of ten ampoules. The nominal absorbances referred to the blank, span a range of 0.3 to 0.9 absorbance units over the four certified wavelengths for a 10 mm pathlength cuvette. Approximately 10 mL of each solution is flame-sealed into an individual glass ampoule, which has been pre-scored for easy opening. The blank and sample solutions are packaged in separate trays.

Certified Values: Table 1 gives the certified values of the apparent net absorbance of SRM 1935a for the indicated wavelengths and a 10.00 mm internal pathlength. The certified values are valid without correction over a temperature range of 20 °C to 24 °C and for an instrumental spectral bandpass not to exceed 2 nm. Measurements should be made immediately after opening the original ampoules, or within the same day for well sealed cuvettes.

Table 1. Certified net apparent absorbance for SRM 1935a at 22 °C ± 2 °C and for a 10.00 mm pathlength

Certified Value of Apparent Absorbance at Indicated Wavelength			
235 nm	257 nm	313 nm	350 nm
0.7455 ± 0.0040	0.8680 ± 0.0050	0.2905 ± 0.0032	0.6456 ± 0.0034

Expiration of Certification: The certification of SRM 1935a is valid, within the measurement uncertainties specified, until **31 December 2014,** provided the SRM is handled and stored in accordance with the instructions given in this certificate. The certified values have been assigned appropriate component uncertainties to account for potential drift. However, the certification is invalid if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The technical measurements leading to the certification of this SRM were performed by M.V. Smith and J.C. Travis with supervisory oversight by S. J. Choquette of the NIST Biochemical Science Division.

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Certificate Issue Date: 05 August 2008

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The statistical design was provided by H-k. Liu of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Source and Preparation of Material: Solutions of 60.20 mg/L of potassium dichromate in 0.001 N perchloric acid and the perchloric acid blank were prepared, ampouled, and labeled by the Biochemical Science Division and the Measurement Services Division of NIST.

NIST Certification Procedure: The optical transmittance measurements were made on the second generation high-accuracy reference spectrometer in the NIST Biochemical Science Division. The spectrophotometer was constructed and calibrated using the principles of the original instrument [2]. An effective spectral bandpass of 0.8 nm was used for all measurements. The wavelength scale of the reference spectrometer was calibrated to an estimated accuracy of ± 0.1 nm. The temperature inside the spectrometer sample chamber was 22 °C ± 1 °C during the certification measurements and was recorded to 0.1 °C before and after each run for correction of the data to 22 °C.

A run-order stratified random sampling was employed to select SRM 1935a Potassium Dichromate, UV Absorbance Standard blank and sample ampoules for certification measurements. Concurrent measurements were made on a like number of control solution ampoules of SRM 1935. Measurements were made in four runs on each of three days. In each run, six solutions were measured in six calibrated SRM 932 Quartz Cuvettes [3] using the normal measurement protocol of the instrument. The order in which the SRM 932 cuvettes were placed in the sample carriage was the same for all 12 runs. One sample of each of the four solutions (SRM 1935a blank, SRM 1935a solution, SRM 1935 blank, and SRM 1935 solution) was run in each cuvette on each day.

Assignment of Uncertainties: Standard uncertainty components, equivalent to the estimated standard deviation for a normal distribution, were assigned for repeatability, temporal drift, temperature uncertainty, instrument spectral bandwidth, and instrument wavelength accuracy. The repeatability component was computed as the estimated standard deviation of the mean of 18 measured net apparent absorbance values. Temporal drift uncertainty was generously estimated from measurements of SRM 1935 over a seven-year period. Temperature related uncertainty was assigned on the basis of the temperature coefficients given under "Temperature Correction" below, to accommodate a temperature range of 22 °C ± 2 °C. The instrument spectral bandwidth and wavelength accuracy were estimated from the full spectrum of SRM 1935a, shown in Figure 1, to accommodate a maximum spectral bandwidth of 2 nm and a wavelength bias of up to ± 1 nm. The standard uncertainty components were combined using the root-sum-of-squares method. An expansion factor of $k = 2$ was applied such that the expanded uncertainties given in Table 1 express an interval within which the true value is expected to fall with a level of confidence of approximately 95 %.

INSTRUCTIONS FOR USE

CAUTION: This SRM is an acid solution contained in tip-sealed borosilicate glass ampoules with pre-scored stems. Therefore, all appropriate safety precautions, including use of gloves during handling, should be taken to avoid accidental breakage or spillage. Unopened ampoules should be stored under normal laboratory conditions in an upright position inside the original container supplied by NIST.

Opening an Ampoule: When an ampoule is to be opened, that area of the stem where the pre-scored band is located should be carefully wiped with a clean, damp cloth and the body of the ampoule wrapped in absorbent material. Then holding the ampoule steady and with thumb and forefinger grasping the stem, **minimal** thumb pressure should be applied to the stem to snap it. Correctly done, the stem should break easily where pre-scored. Use of a metal file to break the stem is **NOT** recommended.

SRM 1935a solutions are to be transferred sequentially to a fused-silica cuvette of known pathlength, b, and the apparent absorbances measured at wavelengths 235 nm, 257 nm, 313 nm, and 350 nm, using a spectral bandpass less than or equal to 2 nm and a wavelength accuracy of at least 1 nm. The temperature of the sample should be determined to ± 1 °C. Clean borosilicate pipettes should be employed to transfer solutions from the ~10 mL ampoules to the ~3 mL cuvette. Each ampoule is intended to supply material for two rinsings of the cuvette prior to transfer of the final portion for measurement. For this purpose, the first aliquot of ~3 mL is transferred from the freshly opened ampoule into an empty and clean cuvette (a liquid height of ~3 cm in a cuvette of 1 cm^2 cross section) and is then removed to waste for proper disposal (see the Material Safety Data Sheet [MSDS] accompanying the SRM). A second aliquot is likewise transferred and removed to waste using the same pipette. A

third and final ~3 mL aliquot is transferred from the ampoule with the same pipette, and the apparent absorbances are measured. Following the measurement, the cuvette is emptied to waste with the same pipette and cleaned using normal laboratory procedures. The second ampoule required for each measurement (one blank and one sample) is treated in like fashion, using a clean pipette to avoid cross contamination. It is recommended that the same cuvette be used in the same orientation for each of the two solutions. Alternatively, two cuvettes that have been optically matched may be employed.

NIST Special Publication 260-54 [4] describes the use of the closely related standard, SRM 935a, and may be consulted for a detailed discussion of solution and cuvette handling issues.

Calculations: The accuracy of the absorbance scale of the spectrometer being tested is ascertained by comparing the measured net apparent absorbances, A(meas), for the four wavelengths to the certified values in Table 1. The net apparent absorbance is given as the measured apparent absorbance of the sample solution, A_s(meas), minus the measured apparent absorbance of the blank solution, A_b(meas):

$$A(\text{meas}) = A_s(\text{meas}) - A_b(\text{meas})$$

If the temperature of the sample chamber during the measurement was outside the temperature range of 20 °C to 24 °C, then the measured data should be corrected to the temperature of certification, 22 °C, using the instructions given below under "Temperature Correction".

To demonstrate that a user's measurements are traceable within acceptable limits to the accuracy defined by SRM 1935a, the user must first determine the required tolerances or acceptable uncertainty for the application in question. Multiple measurements should be made for a given filling of each cuvette, with removal and replacement of the cuvette between measurements. The user should then compare the mean net apparent absorbance and the user-defined tolerance with the certified value and the corresponding expanded uncertainty. An acceptable level of agreement between a user's measurements and the certified value is assured if any part of the range defined by the NIST certified value and its expanded uncertainty overlaps any part of the user's tolerance band defined by the measured mean and the user-defined level of acceptable uncertainty.

Temperature Correction: SRM 1935a may be used as an absorbance standard at temperatures in the range 20 °C to 30 °C provided corrections are made to the A(meas) values. Over this range the net apparent absorbances decrease approximately linearly with increasing temperature for all the wavelengths given in Table 1. The corresponding temperature coefficients, k, for these wavelengths are given in Table 2.

Table 2. Variation of A(meas) with Temperature Over the Range 20 °C to 30 °C

Wavelength	Temperature Coefficient, k
235 nm	$-0.0005\ (°C)^{-1}$
257 nm	$-0.0005\ (°C)^{-1}$
313 nm	$-0.0001\ (°C)^{-1}$
350 nm	$-0.0004\ (°C)^{-1}$

The value of A(meas, T) at any temperature "T" in the range 20 °C to 30 °C can be corrected to the 22 °C certification temperature using the appropriate temperature coefficient and the relation:

$$A(\text{meas}, 22) = A(\text{meas}, T) - k \times (T - 22)$$

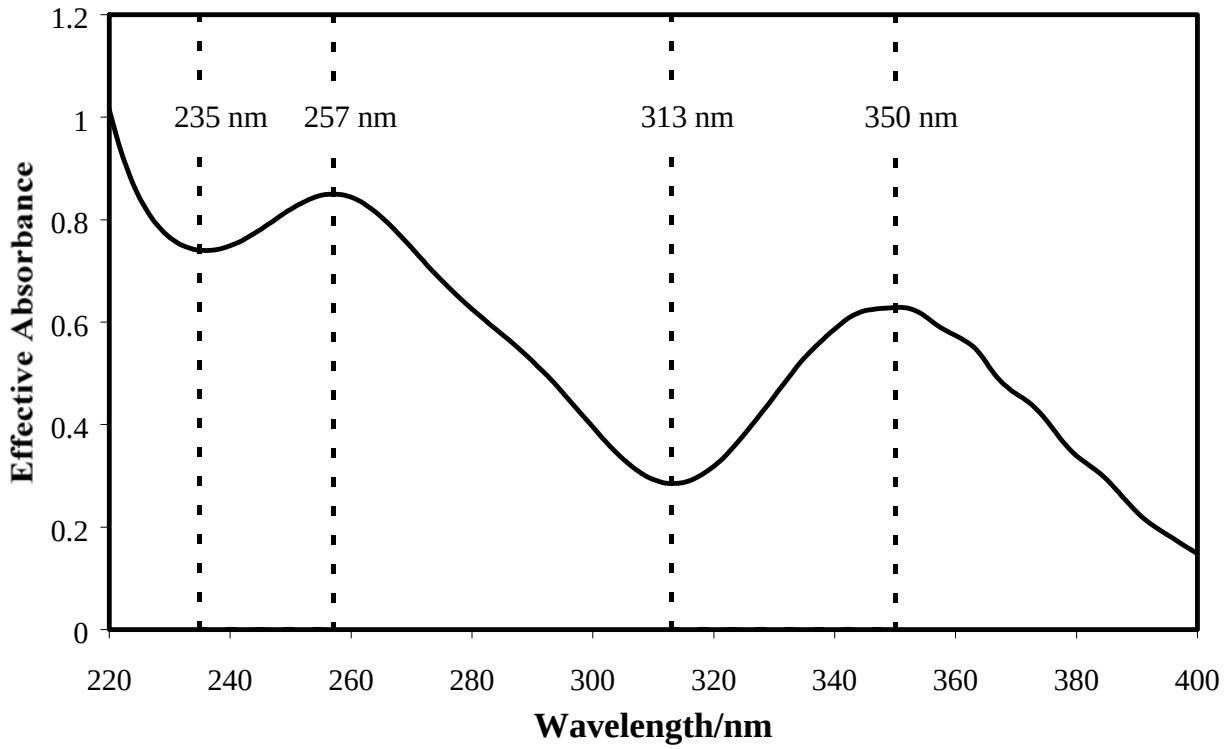

Figure 1. Net absorbance spectrum of SRM 1935a.

REFERENCES

[1] Mielenz, K.D.; *Analytical Chemistry*, Vol. 48, pp. 1093-1094, (1976).

[2] Mavrodineanu, R.; *An Accurate Spectrophotometer for Measuring the Transmittance of Solid and Liquid Materials*; J. Res. Nat. Bur. Stand. (U.S.), Vol 76A (Phys. and Chem.), No. 5, pp. 405-425, 1972.

[3] Mavrodineanu R. and Lazar J. W.; *Standard Reference Materials: Standard Quartz Cuvettes for High Accuracy Spectrophotometry*; NBS Special Publication 260-32, U.S. Government Printing Office: Washington DC (December, 1973).

[4] Burke, R.W. and Mavrodineanu, R.; *Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard*, NIST Special Publication 260-54, 1977. Copies may be obtained via the Internet at: http://ts.nist.gov/MeasurementServices/ReferenceMaterials/upload/SP260-54.PDF

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.