National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 935a

Crystalline Potassium Dichromate
for Use as an Ultraviolet Absorbance Standard

This Standard Reference Material (SRM) is intended for use as a reference standard for the verification of the accuracy and linearity of the absorbance scale at the 235 nm, 257 nm, 313 nm, 345 nm, and 350 nm wavelengths of absorption spectrometers that can provide an effective bandpass of 1.6 nm or less. Such verification is accomplished by comparing the measured apparent absorbances, A_a (meas.), to the calculated absorbances A_h (calc.) from the certified apparent specific absorbance[1] (ε_a) values as described under the Instructions for Use.

SRM 935a consists of 15 g of crystalline potassium dichromate of established purity. Solutions of known concentrations of this SRM in 0.001 N perchloric acid are certified for ε_a at 23.5 °C.

Certified Values: Table 1 gives the certified values of ε_a in $kg \cdot g^{-1} \cdot cm^{-1}$ for ten mass fractions of the SRM 935a potassium dichromate in 0.001 N perchloric acid at 23.5 °C and the indicated wavelengths and spectral bandpass for a 1 cm internal pathlength.

Expiration of Certification: The crystalline form of SRM 935a is stable indefinitely. Solutions prepared from SRM 935a in the mass fraction range indicated in Table 1 and made according to the instructions given in this certificate have been found to be stable within the uncertainties specified in Table 1 for at least six months when stored at room temperature and protected from evaporation and exposure to light.

Source of Material: The crystalline potassium dichromate used for SRM 935a is a special lot of analytical reagent grade material obtained from the J.T. Baker Chemical Co.[2], Phillipsburg, NJ.

Assay: A coulometric assay of the undried material indicated a purity in excess of 99.97 %. In addition, the material was examined by optical emission spectrometry for trace elemental impurities. The only significant impurities detected were sodium and rubidium. Their mass fractions were estimated to be in the range of 0.02 % and 0.03 %, respectively. Drying at 105 °C for 12 hours showed that the surface moisture of this material was less than 0.01 %.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by J.W.L. Thomas.

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Revised Certificate Issue Date: 24 November 2000
See Certificate Revision History on Last Page

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[1]The term "apparent specific absorbance" is used because no corrections have been applied to the absorbance data for the effects of internal multiple reflections within the cuvette or for buoyancy, i.e., the weights used to express mass fractions have not been corrected to vacuum. These combined corrections do not exceed 0.2 %. The specific absorbances are given in reference [1]. The nomenclature used in this certificate is that recommended by K.D. Mielenz [2].

[2]Certain commercial equipment, instruments, or materials are identified in this certificate specify the experimental procedure adequately. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

The sample preparations and technical measurements leading to the certification of this SRM were performed by R.W. Burke of the NIST Analytical Chemistry Division.

Table 1. Apparent Specific Absorbances, ε_a, $kg \cdot g^{-1} \cdot cm^{-1}$

Nominal Mass Fraction $g \cdot kg^{-1}$	Wavelength and (Bandpass) nm					
	235.0(1.2)	257.0(0.8)	313.0(0.8)	345.0(0.8)[a]	350.0(0.8)	Uncertainty[b]
0.020	12.260	14.262	4.805	10.604	10.672	± 0.034
0.040	12.304	14.318	4.811	10.603	10.682	± 0.020[c]
0.060	12.347	14.374	4.816	10.602	10.692	± 0.020[c]
0.080	12.390	14.430	4.821	10.601	10.701	± 0.020[c]
0.100	12.434	14.486	4.827	10.600	10.711	± 0.020[c]

Nominal Mass Fraction $g \cdot kg^{-1}$	Wavelength and (Bandpass) nm					
	235.0(1.6)[d]	257.0(1.6)[d]	313.0(1.6)[d]	345.0(1.6)[d]	350.0(1.6)[d]	Uncertainty[b]
0.120[e]	12.480	14.541	4.835	10.600	10.722	± 0.04[f]
0.140[e]	12.524	14.605	4.840	10.599	10.731	± 0.04[f]
0.160[e]	12.567	14.658	4.846	10.599	10.742	± 0.04[f]
0.180[e]	12.609	14.711	4.851	10.598	10.751	± 0.04[f]
0.200[e]	12.649	14.763	4.856	10.597	10.759	± 0.04[f]

[a] Wavelength 345.0 nm is near one of the two isosbestic points in $HCrO_4^-/Cr_2O_7^{2-}$ spectra. Because it is on the slope of the composite spectrum, reproduction of the ε_a values is dependent on wavelength accuracy. Measurements at this wavelength should be made only for verification of the linearity of the absorbance scale.

[b] ε_a values are not corrected for the effects of internal multiple reflections within the cuvette, nor have the weights been corrected to vacuum. With these two exceptions, each uncertainty given is the 95 % confidence interval of the mean and includes all known systematic errors.

[c] At wavelength 313.0 nm, the uncertainty is reduced to ± 0.010 $kg \cdot g^{-1} \cdot cm^{-1}$.

[d] The increase in spectral bandpass is necessary to obtain an adequate signal. Expected changes in specific absorbance due to this increase do not exceed 1 part in 1,000.

[e] ε_a values are given to the third decimal place to preserve the smooth variation of the data with concentration, although the uncertainties are in the second decimal place.

[f] At wavelength 313.0 nm, the uncertainty is reduced to ± 0.020 $kg \cdot g^{-1} \cdot cm^{-1}$.

NIST Certification Procedure: The preparation and certification of SRM 935a followed the procedures used for the preparation and certification of SRM 935, which are described in detail in NIST Special Publication 260-54 [3]. Briefly, the transmittances, T, of the solutions prepared from the undried, as-received material were measured with a NIST high accuracy spectrophotometer [4].

Calculations of the apparent specific absorbances, ε_a, for each wavelength are accomplished by using the following equation:

$$\varepsilon_a = \frac{D_s - D_b}{b \times c} = \frac{A_a}{b \times c} \tag{1}$$

where ε_a = apparent specific absorbance
A_a = apparent absorbance
D_s = transmittance density of the sample solution, $-\log_{10} T_s$
D_b = transmittance density of the blank solution, $-\log_{10} T_b$
b = internal cuvette pathlength, cm
c = mass fraction of $K_2Cr_2O_7$ solution, $g \cdot kg^{-1}$
T_s = transmittance of the sample solution
T_b = transmittance of the blank solution

INSTRUCTIONS FOR USE

The use of SRM 935a as an absorbance standard requires the careful preparation of a series of solutions of known mass fraction, c, of the potassium dichromate in 0.001 N perchloric acid. These solutions are transferred sequentially to a fused silica cuvette of known pathlength, b, and their apparent absorbances measured at wavelengths 235 nm, 257 nm, 313 nm, and 350 nm, using the spectral bandpass requirements given in Table 1.

NOTE: NIST Special Publication 260-54 [3] should be referred to each time SRM 935a is used.

Drying Instruction: NO drying is required in preparation for use of this material. Use the material as it is received.

Preparation of Solutions: All potassium dichromate solutions are prepared, and are expressed, on a mass fraction basis. Each solution is prepared individually by weighing milligram amounts of the $K_2Cr_2O_7$ to the nearest microgram on a sensitive microbalance. The weighed samples are transferred quantitatively to 1 L volumetric flasks that have been pre-weighed to the nearest 10^{-2} g. The samples are dissolved in 400 mL to 500 mL of distilled water shown to be free of oxidizable impurities[3], and 1 mL of 1 N perchloric acid, prepared from reagent grade material, is added to each to adjust acidity. After diluting approximately to volume with distilled water, the flasks are sealed, and the solutions are mixed well. Tightly fitting stoppers should be used to prevent evaporation. The flasks and contents are weighed again to the nearest 10^{-2} g, and the net weights of the solutions are determined by difference. The concentration of each solution is then calculated and expressed as g/kg $K_2Cr_2O_7$ of solution. A solvent blank is prepared by diluting 1 mL of 1 N perchloric acid to 1 L with distilled water.

Calculation: The accuracy of the absorbance scale of the spectrometer being tested is ascertained by comparing the measured apparent absorbances, A_a (meas.) of a series of 0.001 N perchloric acid solutions containing from 0.020 g to 0.200 g/kg $K_2Cr_2O_7$ to the A_a (calc.) values calculated from the certified ε_a values. Although the ε_a data in Table 1 are given for nominal mass fractions of (0.020, 0.040, 0.060, 0.080, 0.100, 0.12, 0.14, 0.16, 0.18, and 0.20) g $K_2Cr_2O_7$/kg, the ε_a values for the concentrations between these nominal concentrations can be determined by linear interpolation. Using the appropriate ε_a values, the calculated A_a (calc.) values at 23.5 °C are obtained from the expression:

$$A_a = \varepsilon_a \times b \times c \tag{2}$$

An example of the calculation of A_a for one concentration of $K_2Cr_2O_7$ under a specified set of conditions is shown below. Calculations of A_a for other concentrations and wavelengths are performed in a similar manner.

Conditions: Wavelength = 350 nm, spectral bandpass 0.8 nm or less
$b = 0.9982$ cm
$c = 0.04375$ g·kg^{-1}
$t = 23.5$ °C

In Table 1, the ε_a for concentrations of 0.040 g·kg^{-1} and 0.060 g·kg^{-1} are 10.682 and 10.692, respectively. The corresponding ε_a for c = 0.04375 g·kg^{-1} is:

$$\varepsilon_a = 10.682 + \frac{0.0437 - 0.040}{0.060 - 0.040}(10.692 - 10.682)$$

$$\varepsilon_a = 10.682 + 0.0019$$

$$\varepsilon_a = 10.684$$

The calculated apparent absorbance, A_a (calc.), from equation 2, is:

$$A_a \text{ (calc.)} = 10.684 \times 0.9982 \times 0.04375$$

$$A_a \text{ (calc.)} = 0.4666$$

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[3] See Section 6.7 of NIST SP 260-54 [3] for recommended test.

The combined, expanded uncertainty, ΔA_a, in the calculated A_a (calc.) is determined from the uncertainties in ε_a, b, and c in equation 2, combined by the root-sum-of-squares method, provided no other systematic errors are present. Thus:

$$\Delta A_a = \sqrt{[bc\,\Delta\varepsilon_a]^2 + [\varepsilon_a c\,\Delta b]^2 + [\varepsilon_a b\,\Delta c]^2} \qquad (3)$$

To evaluate ΔA_a, $\Delta\varepsilon_a$ is taken from Table 1 and the Δb and Δc values must be determined experimentally or estimated. The Δb and Δc uncertainty components should be expanded to correspond to a level of confidence of 95 %.

Solving equation 3 using hypothetical user-defined relative expanded uncertainties for b and c of 1 part in 10^3 and 2 parts in 10^3, respectively gives:

$$[\Delta A_a]^2 = [1(0.044)\,(0.020)]^2 + [10.7\,(0.044)\,(0.001)]^2 + [10.7(1)\,(0.000088)]^2 = 1.883 \times 10^{-6} \qquad (4)$$
$$\Delta A_a = 0.0014$$

Thus, the uncertainty of A_a, for the above set of conditions, is $\pm\,0.0014$.

To demonstrate that a user's measurements are traceable within acceptable limits to the accuracy defined by SRM 935a, the user must first determine the required tolerances or acceptable uncertainty for the application in question. It is recommended that a number of replicate measurements be made for each mass fraction and wavelength, with removal and replacement of the cuvette between replicate measurements. The user should then compare each mean value and the user-defined tolerance with the absorbance calculated from the certified value using equation (3) and the corresponding expanded uncertainty calculated using equation (4). 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: Although ε_a values in Table 1 are certified at 23.5 °C, SRM 935a can be used as an absorbance standard at other temperatures in the range 20 °C to 30 °C provided corrections are made to the ε_a values. Over this range the apparent specific absorbances decrease 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 ε_a with Temperature Over the Range 20 °C to 30 °C

8, nm	Temperature Coefficient, k % per °C
235	-0.05
257	-0.05
313	-0.02
345	-0.08
350	-0.05

The value of ε_a at any temperature in the range 20 °C to 30 °C can be calculated from the certified value and the appropriate temperature coefficient using the relation:

$$\varepsilon_a^t = \varepsilon_a^{23.5}\left(1 + \frac{k}{100}(t - 23.5)\right) \qquad (5)$$

where: ε_a^t = apparent specific absorbance at temperature t (°C)

$\varepsilon_a^{23.5}$ = apparent specific absorbance certified at 23.5 °C

k = temperature coefficient, % per °C

REFERENCES

[1] Burke, R.W. and Mavrodineanu, R., "Acidic Potassium Dichromate Solutions as Ultraviolet Absorbance Standards," J. Res. Nat. Bur. Stand. (US), **80A** (Phys. and Chem.), No. 4, pp. 631-636 (July-Aug. 1976).

[2] Mielenz, K.D., "Analytical Chemistry," **48**, pp. 1093-1094, (1976).

[3] Burke, R.W. and Mavrodineanu, R., "Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard," NIST Spec. Publ. 260-54, (1977). Copies may be obtained from the Standard Reference Materials Program, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899.

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

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) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.