U.S. Department of Commerce
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National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 935a

Crystalline Potassium Dichromate for Use as an Ultraviolet Absorbance Standard

This Standard Reference Material (SRM) consists of crystalline potassium dichromate of established purity. Solutions of known concentrations of this SRM in 0.001 N perchloric acid are certified for their apparent* specific absorbances**, ε_a, at 23.5 °C.

This SRM is intended to be used as a reference standard for the verification of the accuracy and linearity of the absorbance scale at 235, 257, 313, 345, and 350 nm of absorption spectrometers that can provide an effective spectral bandpass of 1.6 nm or less. Such verification is accomplished by comparing the measured apparent absorbances, A_a, to the A_a calculated from the certified ε_a values as described under "Instructions for Use."

Table 1 (shown on the next page) gives the certified values of ε_a in $kg \cdot g^{-1} \cdot cm^{-1}$ for ten concentrations of the SRM 935a potassium dichromate in 0.001 N perchloric acid at 23.5 °C and the indicated wavelengths and spectral bandpasses for a 1-cm internal pathlength.

The sample preparations and technical measurements leading to the certification of this SRM were performed by R.W. Burke of the Inorganic Analytical Research Division (now retired).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.L. McKenzie.

*The term "apparent" is used because no corrections have been applied to the data for the effects of internal multiple reflections within the cuvette or for buoyancy, i.e., the weights used to express concentrations have not been corrected to vacuum. These combined corrections do not exceed 0.2 percent. The specific absorbances are given in reference 1.

**The nomenclature used in this certificate is that recommended by K.D. Mielenz, Anal. Chem. 48, 1093-1094 (1976), which is reproduced in the Appendix of NBS Special Publication 260-54.

Gaithersburg, MD 20899
April 25, 1988

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

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

Nominal Concentration $g \cdot kg^{-1}$	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]
	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]	
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 $HCrO_4^-/Cr_2O_7^=$ 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 percent confidence interval of the mean and includes all known systematic errors.

[c]At wavelength 313.0 nm, the uncertainty is reduced to ± 0.010.

[d]The increase in spectral bandpass was 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 ± 0.02.

PREPARATION AND CERTIFICATION

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 NBS Special Publication 260-54, Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard[2]. This publication should be referred to every time SRM 935a is to be used. Briefly, the transmittances, T, of the solutions prepared from the undried, as received, material were measured with the NBS Institute for Materials Research high accuracy transmission spectrometer[3].

The ε_a values were calculated for each wavelength using the relation:

$$\varepsilon_a = \frac{D_s - D_b}{b \times c} = \frac{A_a}{b \times c} \qquad (1)$$

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 = concentration, by weight, of $K_2Cr_2O_7$ solution, $g \cdot kg^{-1}$

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., Phillipsburg, N.J.

Assay: A coulometric assay of the purity of the undried material was performed by G. Marinenko of the NBS Center for Analytical Chemistry. The purity was found to be better than 99.97 percent. In addition, the material was examined by optical emission spectrometry for trace elemental impurities by J.A. Norris of the NBS Center for Analytical Chemistry. The only significant impurities detected were sodium and rubidium. Their concentrations were estimated to be in the range of 0.02 and 0.03 weight percent, respectively. Drying at 105 °C for 12 hours showed that the surface moisture of this material was less than 0.01 percent.

Stability: Solutions prepared from SRM 935a in the concentration range indicated in table 1 and made according to the instructions given in NBS SP 260-54 have been found to be stable within the uncertainties given in table 1 for at least six months when stored at room temperature and protected from evaporation and exposure to light.

INSTRUCTIONS FOR USE

The use of SRM 935a as an absorbance standard requires the careful preparation of a series of solutions of known concentrations, c, of the potassium dichromate in 0.001 N perchloric acid. These solutions are transferred sequentially to a quartz cuvette of known pathlength, b, and their apparent absorbances measured at wavelengths 235, 257, 313, and 350 nm, using the spectral bandpass requirements given in table 1. The preparation and measurement of these solutions are described in detail in Section 5 of NBS SP 260-54.

The accuracy of the absorbance scale of the spectrometer being tested is ascertained by comparing the measured apparent absorbances, A_a, of a series of 0.001 N perchloric acid solutions containing 0.020 to 0.200 gram $K_2Cr_2O_7$/kg to the A_a values calculated from the certified ε_a values. Although the ε_a data in table 1 are given for nominal concentrations 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 concentrations between these nominal concentrations can be determined by linear interpolation. Using the appropriate ε_a values, the calculated A_a values at 23.5 °C are obtained from the expression:

$$A_a = \varepsilon_a \times b \times c \qquad (2)$$

Calculations:

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 $g \cdot kg^{-1}$
t = 23.5 °C

From column 6, table 1, the ε_a for concentrations of 0.040 and 0.060 $g \cdot kg^{-1}$ are 10.682 and 10.692, respectively. The corresponding ε_a for c = 0.04375 $g \cdot kg^{-1}$ is:

$$\varepsilon_a = 10.682 + \frac{0.04375 - 0.040}{0.060 - 0.040}(10.692 - 10.682)$$

$$\varepsilon_a = 10.682 + 0.0019$$

$$\varepsilon_a = 10.684$$

The calculated apparent absorbance, A_a, from equation 2, is:

$$A_a = 10.684 \times 0.9982 \times 0.04375$$

$$A_a = 0.4666$$

The uncertainty, ΔA_a, in the calculated A_a is determined from the combined uncertainties in ε_a, b and c in equation 2, provided no other systematic errors are present. Thus:

$$\Delta A_a = bc|\Delta\varepsilon_a| + \varepsilon_a c|\Delta b| + \varepsilon_a b|\Delta c| \qquad (3)$$

To evaluate ΔA_a, $\Delta\varepsilon_a$ is taken from column 7 of table 1 and the Δb and Δc values must be determined experimentally.

In the experiments performed to obtain the ε_a values in table 1, the uncertainties for b and c did not exceed 1 part in 10^4 and 2 parts in 10^4, respectively.

The solution of equation 3 gives:

$$\Delta A_a = 1(0.044)\ (0.020) + 10.7(0.044)\ (0.0001) + 10.7(1)\ (0.0000088)$$
$$= 0.0010$$

Thus, the uncertainty of A_a, for the above set of conditions, is ± 0.0010.

The correction of the absorbance scale of the absorption spectrometer under test is determined by plotting the differences between A_a measured and A_a calculated as a function of absorbance. A typical plot of such a graph is shown in figure 1. The apparent absorbances measured on this instrument at 350 nm are accurate when the indicated correction is subtracted from the corresponding absorbance scale reading, provided that the conditions of wavelength accuracy, spectral bandpass, and absence of stray light are fulfilled as specified in NBS SP 260-54. Correction curves for wavelengths 235, 257, and 313 nm are obtained in a similar manner.

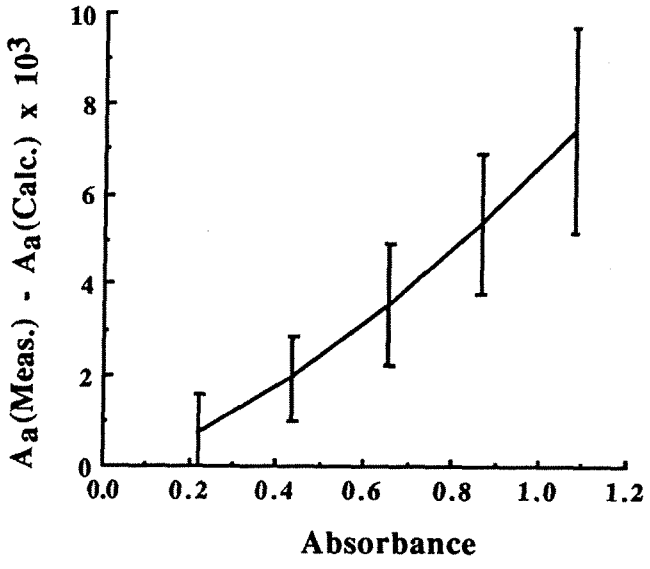

Figure 1. Correction curve for the absorbance scale of a precision spectrometer. The error bars are the sum of the errors arising from the uncertainties in the certified apparent specific absorbances, ε_a, cuvette pathlength, b, and concentration, c.

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 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 to 30 °C.

λ, nm	Temperature Coefficient, k Percent per degree Celsius
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 to 30 °C can be calculated from the certified value and the appropriate temperature coefficient using the relation:

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

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, percent per °C.

ACKNOWLEDGEMENTS:

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REFERENCES:

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

2. Burke, R.W., and Mavrodineanu, R., Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard, NBS Spec. Publ. 260-54 (1977). Copies may be obtained from the Office of Standard Reference Materials, National Bureau of Standards, Gaithersburg, MD 20899.

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