

# National Bureau of Standards

## Certificate

### Standard Reference Material 2033

#### Crystalline Potassium Iodide with Attenuator Heterochromatic and Isochromatic Stray Radiant Energy Standard for Ultraviolet Absorption Spectrophotometry

K. D. Mielenz and R. Mavrodineanu

This Standard Reference Material consists of reagent-grade crystalline potassium iodide (KI) and a radiation attenuator to be used to assess the heterochromatic stray radiant energy (stray light) in ultraviolet absorption spectrophotometers in the spectral region below 260 nm. The radiation attenuator consists of two semitransparent evaporated metal-on-fused silica (non-fluorescent) filters, each having a nominal transmittance of 10%. One filter is mounted in a cuvette-style holder that can be inserted into the sample compartment of the spectrophotometer. The other is mounted in one of the two shutters of the holder. The use of this attenuator permits the expansion of the transmittance scale into the low-transmittance region by providing a two-step attenuation of the reference beam of the spectrophotometer to about 1%. The attenuator can also be used to assess isochromatic stray light by following the instructions given in this certificate.

The heterochromatic stray light is assessed by measuring the spectral absorbance of aqueous solutions of SRM 2033 of known pathlengths and concentrations, and comparing the results with the certified values of the specific absorbance,  $\epsilon$ .

#### Specific Absorbance<sup>a</sup>

$\lambda$	$\epsilon$ ( $L g^{-1} cm^{-1}$ ), vs Wavelength, $\lambda$ (nm), at 23.5 °C							
	240	245	250	255	260	265	270	275
$\epsilon$	25.6	10.67	3.66	1.05	0.260	0.0560	0.0121	0.0031

<sup>a</sup>"Specific Absorbance" is defined here as absorbance per unit pathlength and unit concentration. The term "absorptivity" has been avoided since it is ambiguously defined. See K. D. Mielenz, *Anal. Chem.* **48**, 1093-1094 (1976).

The estimated uncertainty of these values is  $\pm 5\%$ , which includes the random and systematic errors of the calibration procedure, as well as variations due to possible instability of the KI. (See Certification Procedure.)

The material used to produce SRM 2033 was obtained from the J.T. Baker Chemical Co., Phillipsburg, N.J., in two bottles, as reagent-grade (99.8% purity) potassium iodide.

The transmittance of the filter mounted in the holder at  $\lambda 255$  nm is \_\_\_\_\_ ;  
the transmittance of both filters at  $\lambda 255$  is \_\_\_\_\_.

SRM 2033 was issued with the technical assistance of J. R. Baldwin, R. W. Burke, A. L. Cummings, B. I. Diamondstone, and G. A. Sleater, and under the overall direction of E. L. Garner, NBS Inorganic Analytical Research Division.

The technical and support aspects concerning preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by R. W. Seward.

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George A. Uriano, Chief  
Office of Standard Reference Materials

(over)

#### Potassium Iodide Material Testing:

Material homogeneity was tested by measuring the absorbance of 1% aqueous solutions of the KI sampled from the top, middle, and bottom of each bottle. These measurements, at 265, 267, and 270 nm, showed no evidence of inhomogeneity. Tests for moisture content (Karl Fischer method) gave an average of 0.007%. This value was sufficiently small that all certified data are based on weighed samples of the undried, as received, material.

Stability of the material to UV and visible light was tested by exposing the KI salt in a low-actinic glass bottle to radiation from a 3 kW xenon-arc lamp at a distance of 25 cm for four days at room temperature. The average absorbances at five wavelengths between 240 and 270 nm of aqueous solutions of the exposed material were 1.1% lower than those of solutions of the unexposed material. In view of the severity of this test, this change was considered minor. Nonetheless, the 1.1% was included in the overall uncertainty of the certified values.

#### Potassium Iodide Certification Procedure:

The certified specific absorbances were measured in the NBS Center for Analytical Chemistry high-accuracy spectrophotometer [1,2], equipped with a deuterium lamp and UV averaging sphere [3,4]. Thirteen aqueous solutions of KI with concentrations ranging from 0.03 to 30 g L<sup>-1</sup> were prepared and measured against distilled water, using standard fused-silica cuvettes with pathlengths between 10.001 and 10.009 mm<sup>b</sup>. The absorbance measurements were performed at the temperature,  $t = 23.5 \pm 0.5^\circ\text{C}$ . A 0.2 nm bandpass was used, and wavelength settings were made with an accuracy of 0.05 nm. The measurements were made on at least three concentrations at each wavelength. These concentrations were chosen so that most absorbance readings fell between 0.1 and 1.0 to minimize stray light and bandwidth errors. The data were found to obey Beer's law.

Thus, the equation,

$$\epsilon = A/c\ell \quad (1)$$

was used to calculate the specific absorbances,  $\epsilon$ , from the measured absorbances,  $A$ , and the known values of concentration,  $c$ , and pathlength,  $\ell$ .

Limits to random error (two standard deviations) of these measurements (including the photometric imprecision of the spectrophotometer, errors in the repositioning of cuvettes, concentration errors, pathlength uncertainties, temperature errors, Beer's law uncertainties, and bandwidth errors) were determined to be  $\pm 2.4\%$ . The error due to the 0.05 nm uncertainty of the wavelength calibration of the spectrophotometer is  $\pm 1.1\%$ .

The uncertainty of 5% stated on the face of this certificate represents the sum of these errors and the above mentioned 1.1% uncertainty due to instability of the KI. No corrections were applied for the effects of internal reflections inside the sample and reference cuvettes, nor were the weights corrected to vacuum. These and all other sources of error were considered negligible.

The temperature coefficient at 260 nm was determined to be

$$\frac{1}{\epsilon} \cdot \frac{d\epsilon}{dt} = 0.031^\circ\text{C}^{-1}. \quad (2)$$

For precision measurements, it is recommended that SRM 2033 be used in thermostated cuvettes at 23.5 °C, or that a temperature correction according to Eq. (2) be applied.

<sup>b</sup>Issued by NBS as SRM 932, Quartz Cuvette for Spectrophotometry.

## Instructions for Use of Potassium Iodide

### Storage and Preparation:

SRM 2033 should be stored in the original, low-actinic glass bottle and the cardboard container in which it was issued to protect it from unnecessary exposure to light and humidity. When so stored, the expected stability of this material is at least three years. Thus, until additional stability data are obtained, this material should be used within three years of the date of purchase.

All solutions prepared from SRM 2033 should be made in borosilicate glass containers using distilled water and transfer pipettes (Pasteur type) of the same glass and fitted with rubber bulbs<sup>6</sup>. Use clean spectrophotometer cuvettes, free of scratches, made of non-fluorescent fused silica, and fitted with ground-glass or Teflon stoppers to minimize evaporation; or preferably use NBS SRM 932. Mark all cuvettes to assure the same orientation in the spectrophotometer, and place them into their respective holders. Using transfer pipettes of the type mentioned, rinse each cuvette several times with distilled water. Prepare a solution of KI in distilled water (e.g., 1%), fill the sample cuvette with the KI solution and the reference cuvette with distilled water. Measure the absorbance, leaving the cuvettes in their holders, empty them (using the pipettes), and repeat the rinsing and filling operations until constant absorbance readings are obtained. Fresh solutions should be made before every test.

### Measurements:

A 1% KI solution ( $c = 10 \text{ g L}^{-1}$ ) with a 1 cm pathlength exhibits a sharp cutoff in transmittance near 260 nm; i.e., it transmits more than 90% above 273 nm, but less than 0.01% below 258 nm. Therefore, with the monochromator set for a wavelength below 260 nm, any appreciable amount of light detected is heterochromatic stray light, which consists of wavelengths above the cutoff. The amount of stray light in the spectrophotometer at wavelength  $\lambda$  may be determined from the equations:

$$T'(\lambda) = \frac{T(\lambda) + x(\lambda)}{1 + x(\lambda)} \quad (3)$$

$$x(\lambda) = \frac{T'(\lambda) - T(\lambda)}{1 - T'(\lambda)} \quad (4)$$

where:

$x(\lambda)$  is the stray light ratio,

$T'(\lambda)$  is the apparent transmittance,

$T(\lambda)$  is the true transmittance.

The stray light ratio,  $x(\lambda)$ , is the proportion of heterochromatic stray radiant energy in the spectrophotometer for the wavelength setting  $\lambda$ . Equation (4) forms the theoretical basis for the determination of the stray light ratio by comparing apparent transmittance to true transmittance. For SRM 2033, the true transmittance,  $T(\lambda)$ , of KI solutions may be calculated as:

$$T(\lambda) = 10^{-\epsilon(\lambda) c \ell}$$

where  $\epsilon(\lambda)$  is the certified specific absorbance given on the face of this certificate.

<sup>6</sup>Soft glass containers and pipettes contain residual amounts of UV absorbing material, but can be used after proper cleaning. Several rinses, first with isopropyl alcohol and then with distilled water, are generally adequate.

The apparent transmittances of KI solutions depend not only on the stray light ratio of the spectrophotometer, but also on the wavelength accuracy and the spectral bandwidth, which can significantly affect the results obtained because of the steep slope of the absorbance cutoff of KI. A low-pressure mercury discharge lamp is suggested for verifying the wavelength scale, and a bandwidth as narrow as compatible with adequate signal-to-noise ratios should be used.

#### Optical Attenuator:

Many instruments do not permit the direct measurement of transmittances below certain limits, e.g., 1% or 0.1%. To measure stray light ratios below these limits, the reference beam of the spectrophotometer must be attenuated to extend the transmittance scale into the low-transmittance region.

As mentioned on the face of this Certificate, the optical attenuator consists of two filters, each of which has a nominal transmittance of 10 percent. One filter is mounted in a metal holder that can be inserted in the sample compartment of the spectrophotometer (5). This holder is provided with a front and rear shutter, one of which has a window in which the second filter is mounted. The holder and shutters are flat black. This unit was produced in the NBS Instrument Shops.

#### Instructions for Use of the Attenuator

This unit can be used to attenuate the incident radiation in the reference beam of the spectrophotometer in two steps by a total factor of about 100, corresponding to about 1 percent transmittance (6). To attenuate by a factor of 10, the attenuator is inserted in the sample compartment of the spectrophotometer facing the incident beam, with both shutters removed. A further attenuation by a factor of about 10 is obtained when the shutter carrying the second filter is inserted in the holder, in front of the first filter. Under these conditions, and with an instrument that cannot measure transmittances lower than 1 percent, the use of the attenuator will permit heterochromatic stray light to be measured down to about 0.01 percent. This attenuation procedure can be used with spectrophotometers capable of scale expansion.

#### Isochromatic Stray Light:

The radiation attenuator can be used to assess the isochromatic stray light that results from reflection of the incident radiation at the surface of the sample and various optical components, and reaches the photodetector without passing through the sample. It is implicitly assumed that the sample compartment of the spectrophotometer is light-tight.

The measurement is performed by placing the attenuator in the sample beam of the spectrophotometer, with the opaque shutter placed at the rear of the filter holder. Under these conditions, if a signal is detected, it is caused by reflection at the surface of the filter exposed to the incident radiation. This radiation is scattered from the walls and other components of the sample compartment and reaches the photodetector without passing through the sample (5). This signal is the isochromatic stray light.

Isochromatic stray light, which passes through the sample, is generally caused by interreflections between lenses and/or other sample compartment elements. Tests for this stray light component, which is not detected by the methods described above, are discussed in references 7 and 8.

#### References:

1. R. Mavrodineanu, J. Res. NBS 76A, 405-425 (1972).
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3. K. D. Mielenz, R. Mavrodineanu, and E. D. Cehelnik, J. Res. NBS 78A, 631-635 (1974).
4. K. D. Mielenz, R. Mavrodineanu, and E. D. Cehelnik, Appl. Optics 14, 1940-1947 (1975).
5. R. Mavrodineanu, J. Res. NBS 80A, 637-641 (1976).
6. Estimating Stray Radiant Energy, ASTM Manual on Recommended Practices in Spectrophotometry, pp. 94-105, 3rd. Edition, 1969, 1916 Race St., Philadelphia, Pa. 19103.
7. K. D. Mielenz, J. Res. NBS 76A, 455-467 (1972).
8. K. D. Mielenz and R. Mavrodineanu, J. Res. NBS 77A, 699-703 (1973).