

National Bureau of Standards

Certificate

Standard Reference Material 2032

Crystalline Potassium Iodide

Heterochromatic Stray Radiant Energy Standard for Ultraviolet Absorption Spectrophotometry

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This Standard Reference Material consists of reagent-grade, crystalline potassium iodide (KI) to be used to assess heterochromatic stray radiant energy (stray light) in ultraviolet absorption spectrophotometers in the spectral region below 260 nm. Stray light is assessed by measuring the spectral absorbance of aqueous solutions of SRM 2032 of known pathlengths and concentrations, and comparing the result with the certified values of the specific absorbance, ϵ .

Specific Absorbance ^a								
ϵ (L g ⁻¹ cm ⁻¹), vs Wavelength, λ (nm), at 23.5 °C								
λ	240	245	250	255	260	265	270	275
ϵ	25.6	10.67	3.66	1.05	0.260	0.0560	0.0121	0.0031

^a"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 2032 was obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J., in two bottles, as reagent-grade (99.8% purity) potassium iodide.

SRM 2032 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 I. L. Barnes.

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

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Supplementary Information

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.

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⁻¹ were prepared and measured against distilled water, using standard fused-silica cuvettes with pathlengths between 10.001 and 10.009 mm^b. The absorbance measurements were performed at the temperature, $t = 23.5 \pm 0.5$ °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, ϵ , from the measured absorbances, A , and the known values of concentration, c , and pathlength, ℓ .

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

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

For precision measurements, it is recommended that SRM 2032 be used in thermostated cuvettes at 23.5 °C, or that a temperature correction according to Eq. (2) be applied.

^bIssued by NBS as SRM 932, Quartz Cuvettes for Spectrophotometry.

Instructions for Use

Storage and Preparation:

SRM 2032 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 2032 should be made in borosilicate glass containers using distilled water and transfer pipettes (Pasteur type) of the same glass and fitted with rubber bulbs^c. 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 λ 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 λ . Equation (4) forms the theoretical basis for the determination of the stray light ratio by comparing apparent transmittance to true transmittance. For SRM 2032, the true transmittance, $T(\lambda)$, of KI solutions may be calculated as:

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

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

^cSoft 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.

Many instruments do not permit the direct measurement of transmittances below certain limits, e.g., 1% or 0.1%. For such instruments, the use of SRM 2032 will only measure stray light ratios above these limits. 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.

References

1. R. Mavrodineanu, *J. Res. NBS* **76A**, 405-425 (1972).
2. J.F. Barkley, F. C. Rugg, and R. Mavrodineanu, 29th Pittsburgh Conf., Abstract 452, Cleveland, Ohio, (1978).
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).