The Calibration of Scanning Monochromators for the Measurement of Absolute Irradiance

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Certain approximations commonly used in the absolute calibration of a scanning monochromator are examined in terms of the response of the instrument to a monochromatic input. The absolute irradiance due to any spectral feature in the neighborhood of λ_0 is commonly computed from the expression $W = AB(\lambda_0)/H(\lambda_0)$, where A is the area of the spectral feature as recorded by the monochromator output trace, $B(\lambda)$ is the spectral irradiance of a standard source, and $H(\lambda)$ is the response of the monochromator to $B(\lambda)$ when the monochromator corresponds to wavelength λ. As an example, approximations used in justifying such calculations are examined and applied to an Ebert 0.5-m monochromator. For the case chosen, the approximation is shown to be valid to an accuracy of 1.5% to 2%, depending upon assumptions made in the calculation. It is found that the most serious error for this example is introduced by changes in the sensitivity of the monochromator over a wavelength interval comparable with that of the spectral feature under investigation. A second source of error is found to be the change in the irradiance of the standard source over a wavelength interval comparable to the instrument resolving power.

Introduction

A common spectroscopic problem is the determination of the relative or absolute irradiance of various spectral components of a radiating source. The spectral components may be a set of relatively monochromatic atomic emission lines, more polychromatic molecular emission bands, continuous emissions from hot bodies, or combinations of these three types.

The spectral irradiance may be determined by separating the incoming radiation into its spectral components by the use of a spectrometer or monochromator. The intensity due to each component is then measured by the system detector. This simple solution is complicated by the fact that the response of the spectrometer or monochromator is not the same for all wavelengths of incident radiation. The detector output, whether it is film density, phototube current, or any other measured quantity, will be different for equally intense monochromatic incident radiations of different wavelengths. To overcome this difficulty, it is common practice to calibrate the spectrometer by recording the detector response to a known irradiance, such as the blackbody standard source operating at a known temperature. The standard technique is to measure the area of the spectral feature as recorded by the monochromator in scanning the relevant wavelengths. This area is multiplied by a calibration factor obtained as the ratio of the standard source irradiance at some wavelength, representative of the spectral feature, and the monochromator response to the standard source when the monochromator is set to the same representative wavelength.

There are certain approximations involved in such a computation, most of which arise because of the finite resolution of the instrument. The monochromator will respond to a monochromatic input at a range of instrument settings around the nominal wavelength. This leads, of course, to the finite recorded area of a sharp spectral line. During the calibration procedure, however, the instrument setting is constant; but the response is due to radiations from the continuous source with a range of wavelengths centered around the nominal instrument setting.

The purpose of this article is to examine the validity of using the second of these measurements to calibrate the first. This may be done by considering the monochromator as a linear filter, an approach that has been used profitably in many calculations involving resolution, absorption, and line shape.[1,2] The theory will be developed for the general case and then applied, as an example, to the calibration of a 4000-Å line using an Ebert 0.5-m monochromator.

The General Case

Let $T(\lambda, \Lambda)$ be defined as the response of an instru-

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Received 15 April 1966.

This work was supported by Air Force Cambridge Research Laboratories.

ment to a monochromatic input, $\delta(\lambda' - \lambda)$, when the instrument is set at Λ. Further, let λ_0 be the wavelength for which $T(\lambda, \Lambda_0)$ is a maximum. For some instruments it may be more useful to define λ_0 as the *centroid* of $T(\lambda, \Lambda_0)$, or as the midpoint of the chord connecting the two points of $T(\lambda, \Lambda_0)$ which are half the maximum, or some other way of defining the *center* of $T(\lambda, \Lambda_0)$. The general development that follows is valid for any such choice.

The instrument response to an input $G(\lambda)$ (representing the spectral irradiance of the spectral feature under investigation) as a function of the instrument setting is

$$F(\Lambda) = \int_0^\infty G(\lambda)\, T(\lambda, \Lambda) d\lambda. \tag{1}$$

In these terms, the total irradiance of the spectral feature is

$$W = \int_0^\infty G(\lambda) d\lambda; \tag{2}$$

and the area of the feature as recorded by the instrument is

$$\begin{aligned} A &= \int_0^\infty F(\Lambda) d\Lambda = \int_0^\infty \int_0^\infty G(\lambda)\, T(\lambda, \Lambda) d\lambda d\Lambda \\ &= \int_0^\infty G(\lambda)\, I(\lambda) d\lambda, \end{aligned} \tag{3}$$

where

$$I(\lambda) = \int_0^\infty T(\lambda, \Lambda) d\Lambda. \tag{4}$$

Note that $I(\lambda)$ is the area under the curve of the monochromator output vs monochromator wavelength setting with a monochromatic input of unit intensity and wavelength λ.

With the instrument set at Λ_0 (representing a characteristic wavelength of the feature being considered), the instrument response to the standard source is

$$H(\Lambda_0) = \int_0^\infty B(\lambda)\, T(\lambda, \Lambda_0) d\lambda, \tag{5}$$

where $B(\lambda)$ is the spectral irradiance due to the standard.

A and $H(\Lambda_0)$ are the experimentally measured quantities, and $B(\lambda)$ may be assumed to be known, either from theoretical calculations or from prior calibration. From these, it is hoped that W, the irradiance of the spectral feature, may be estimated. To this end, it may be noted that $I(\lambda)$ and $B(\lambda)$ are slowly varying functions of λ. That is, the changes in $I(\lambda)$ and $B(\lambda)$ will be small over the wavelength interval for which $G(\lambda)$ and $T(\lambda, \Lambda_0)$ have significant value. If we set

$$\begin{aligned} I(\lambda) &= I(\lambda_0) + [I(\lambda) - I(\lambda_0)] \\ &= I(\lambda_0) + \Delta I(\lambda), \end{aligned} \tag{6}$$

and

$$\begin{aligned} B(\lambda) &= B(\lambda_0) + [B(\lambda) - B(\lambda_0)] \\ &= B(\lambda_0) + \Delta B(\lambda), \end{aligned} \tag{7}$$

the integrals representing the experimental measurements become

$$\begin{aligned} A &= \int_0^\infty G(\lambda)\, I(\lambda_0) d\lambda + \int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda \\ &= I(\lambda_0) \int_0^\infty G(\lambda) d\lambda + \int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda \\ &= W I(\lambda_0) + \int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda, \end{aligned} \tag{8}$$

and

$$\begin{aligned} H(\Lambda_0) &= \int_0^\infty B(\lambda_0)\, T(\lambda, \Lambda_0) d\lambda + \int_0^\infty \Delta B(\lambda)\, T(\lambda, \Lambda_0) d\lambda \\ &= B(\lambda_0) \int_0^\infty T(\lambda, \Lambda_0) d\lambda + \int_0^\infty \Delta B(\lambda)\, T(\lambda, \Lambda_0) d\lambda. \end{aligned} \tag{9}$$

Equation (8) may be solved for W, the desired irradiance, using the definition of $I(\lambda)$ from Eq. (4), with the result that

$$\begin{aligned} W &= \frac{A - \int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda}{\int_0^\infty T(\lambda_0, \Lambda) d\Lambda} \\ &= \left[\frac{A - \int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda}{\int_0^\infty T(\lambda, \Lambda_0) d\lambda} \right] \left[\frac{\int_0^\infty T(\lambda, \Lambda_0) d\lambda}{\int_0^\infty T(\lambda_0, \Lambda) d\Lambda} \right]. \end{aligned} \tag{10}$$

The numerator in the last term on the right-hand side of Eq. (10) is the instrument response, when set at Λ_0, to white light of unit intensity. The demoninator is the area of the curve of monochromator output vs monochromator setting with a monochromatic input of unit intensity and wavelength λ_0. For many situations, these terms are nearly equal, so their ratio is almost unity. The integral in the denominator of the first term on the right-hand side of Eq. (10) may be eliminated by using Eq. (9), with the result that

$$\begin{aligned} W = B(\lambda_0) &\left[\frac{A - \int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda}{H(\Lambda_0) - \int_0^\infty \Delta B(\lambda)\, T(\lambda, \Lambda_0) d\lambda} \right] \\ &\times \left[\frac{\int_0^\infty T(\lambda, \Lambda_0) d\lambda}{\int_0^\infty T(\lambda_0, \Lambda) d\Lambda} \right]. \end{aligned} \tag{11}$$

Expanding the expression to first order in the correction terms $\Delta I(\lambda)$ and $\Delta B(\lambda)$ yields.

$$\begin{aligned} W = A \frac{B(\lambda_0)}{H(\Lambda_0)} &\left[\frac{\int_0^\infty T(\lambda, \Lambda_0) d\lambda}{\int_0^\infty T(\lambda_0, \Lambda) d\Lambda} \right] \left[1 - \frac{\int_0^\infty G(\lambda)\, \Delta I(\lambda) d\lambda}{A} \right. \\ &\left. + \frac{\int_0^\infty \Delta B(\lambda)\, T(\lambda, \Lambda_0) d\lambda}{H(\Lambda_0)} \right]. \end{aligned} \tag{12}$$

Thus,

$$W \approx A[B(\lambda_0)/H(\Lambda_0)] \tag{13}$$

is a reasonable estimate for the total irradiance of the spectral feature if, and only if, the obvious approximations to the right-hand side of Eq. (12) can be justified. This is the expression commonly used for such computations.

The approximations used in justifying the use of Eq. (13) instead of Eq. (11) are not generally valid, and should be evaluated for each experimental situation, as is done in the next section for a typical case.

Example

As a typical case we consider an Ebert 0.5-m monochromator with a distance between entrance and exit slits of about 8 cm and a grating ruled with 11,800 lines/cm. In this type of instrument, the light from the entrance slit is collimated, dispersed, and focused on the exit slit. The light from a monochromatic source forms a single image of the entrance slit (for each grating order) which is moved past the exit slit by either a change in grating position or wavelength. If we assume that the optical system and detector have a flat response over a wavelength interval large enough to include $T(\lambda, \Lambda)$ either with λ = constant or with Λ = constant, the transmission of the instrument will be proportional to the overlap of the image of the entrance slit (image width $\approx 2a$) and the exit slit (width $= 2a$). This simple expression should then be multiplied by a slowly varying function of wavelength $g(\lambda)$ representing the wavelength dependence of detector sensitivity and reflection coefficients of the various optical elements.

Letting x_0 be the distance between the center of the image and the center of the exit slit,

$$T(\lambda, \Lambda) = g(\lambda) \int_{-a}^{a} D(x - x_0)dx, \tag{14}$$

where $D(x - x_0)$ is the intensity distribution of the image of the entrance slit.

To find an explicit expression for $x_0(\lambda, \Lambda)$ we must consider the geometry of the monochromator. The angles used are defined in Fig. 1. The angle ϕ is fixed as the angle between a ray passing through the center of the entrance slit and the ray passing through the center of the exit slit. The following relations obtain

$$\alpha + \phi/2 = i, \tag{15}$$

$$\alpha - \beta = \theta, \tag{16}$$

$$d(\sin i + \sin\theta) = n\lambda, \tag{17}$$

where d is the grating constant, and n is the order of diffraction.

For the Ebert geometry, if $\gamma = \beta - \phi/2$,

$$x_0 = f \tan\gamma \approx f\gamma, \tag{18}$$

where f is the focal length of the spectrometer mirror, and γ is assumed to be small.

By substituting Eqs. (15) and (16) into Eq. (17), the following relation is obtained (for first order):

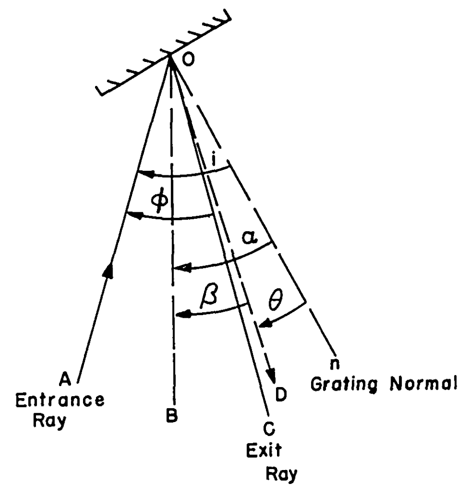

Fig. 1. Monochromator geometry. The vector AO represents the direction of the entrance ray incident upon the grating at O. OC represents the direction of exit rays which are focused on the exit slit. OB is the bisector of the angle AOC. Incident radiation with wavelength λ will be diffracted in the direction OD, which will coincide with OC when the monochromator setting, represented by the angle α, corresponds to λ.

$$\sin(\alpha + \phi/2) + \sin(\alpha - \beta) = \lambda/d, \tag{19}$$

or

$$\sin\alpha \cos(\phi/2) + \cos\alpha \sin(\phi/2) + \sin\alpha \cos\beta - \cos\alpha \sin\beta = \lambda/d. \tag{20}$$

For $\beta = \phi/2$ (which implies $\lambda = \Lambda$), this expression reduces to

$$2 \cos(\phi/2) \sin\alpha = \Lambda/d. \tag{21}$$

Expanding Eq. (19) in terms of γ,

$$\sin\alpha \cos(\phi/2) + \cos\alpha \sin(\phi/2) + \sin(\alpha - \phi/2)\cos\gamma - \cos(\alpha - \phi/2) \sin\gamma = \lambda/d. \tag{22}$$

By making the approximations $\cos\gamma = 1$ and $\sin\gamma = \gamma$, and substituting Λ/d for $2 \cos(\phi/2) \sin(\alpha)$ from Eq. (21), Eq. (22) may be reduced to

$$(\Lambda - \lambda)/d = \gamma \cos(\alpha - \phi/2), \tag{23}$$

which gives

$$\gamma = (\Lambda - \lambda)/[d \cos(\alpha - \phi/2) \tag{24}$$

Using this result, the integrals in the first term on the right-hand side of Eq. (12) may now be written explicity as

$$\int_0^\infty T(\lambda, \Lambda_0)d\lambda = \int_0^\infty g(\lambda) \int_{-a}^{+a} D\left(x - \frac{f(\Lambda_0 - \lambda)}{d \cos(\alpha_0 - \phi/2)}\right)dx\, d\lambda. \tag{25}$$

and

$$\int_0^\infty T(\lambda_0, \Lambda)d\Lambda = \int_0^\infty g(\lambda_0) \int_{-a}^{+a} D\left(x - \frac{f(\Lambda - \lambda_0)}{d \cos(\alpha - \phi/2)}\right)dx\, d\Lambda. \tag{26}$$

The integrals may be put into similar form by substituting

$$y = \frac{f(\Lambda_0 - \lambda)}{d\cos(\alpha_0 - \phi/2)}, \qquad dy = \frac{-fd\lambda}{d\cos(\alpha_0 - \phi/2)}, \tag{27}$$

into Eq. (25) and

$$Z = [f(\Lambda - \lambda_0)/d\cos(\alpha - \phi/2)],$$

$$dZ = fd\Lambda/d\left\{[\cos(\alpha - \phi/2)]^{-1} + \frac{(\Lambda - \lambda_0)\sin(\alpha - \phi/2)}{2d\cos^2(\alpha - \phi/2)\cos(\phi/2)\cos\alpha}\right\}, \tag{28}$$

into Eq. (26).

The limits are set by observing that, in both integrations, the entire range for which T has nonzero values is covered, the only difference being in the direction. Reversing the sign of Eq. (25) and exchanging the limits, the integrals of Eqs. (25) and (26) may be written as

$$\int_0^\infty T(x, \Lambda_0)d\lambda = \frac{d}{f}\int_{-\infty}^{+\infty} g(y)\int_{-a}^{+a} D(x - y)\cos(\alpha_0 - \phi/2)dx\,dy \tag{29}$$

and

$$T(\lambda_0, \Lambda)d\Lambda = \frac{d}{f}\int_{-\infty}^{+\infty} g(y_0)\int_{-a}^{+a} D(x - z)\left\{[\cos(\alpha - \phi/2)]^{-1} + \frac{(\Lambda - \lambda_0)\sin(\alpha - \phi/2)}{2d\cos^2(\alpha - \phi/2)\cos\phi/2\cos\alpha}\right\}^{-1} dx\,dz. \tag{30}$$

Numerical evaluation of the two terms in brackets in Eq. (30) at a wavelength λ_0 of 4000 Å over a wavelength interval of 20 Å gives, for the monochromator described ($\alpha \approx 14°$, $\phi/2 \approx 4°30'$, $\gamma \leq 3'$),

$$[\cos(\alpha_0 - \phi/2)]^{-1} = 1.01 \tag{31}$$

and

$$\frac{|(\Lambda - \lambda_0)|\sin(\alpha - \phi/2)}{2d\cos^2(\alpha - \phi/2)\cos(\alpha/2)\cos\alpha} \leq 2.03 \times 10^{-3}. \tag{32}$$

Thus, Eq. (32) may be neglected in comparison with Eq. (31).

The remaining problems in comparing the integrals are the variation of $\cos(\alpha\text{-}\phi/2)$, which changes with Λ but not with λ, and the variation of $g(\lambda)$, which varies with λ but not with Λ. The evaluation can be made by noting that

$$y_{\min}\int f(x)dx \leq \int y(x)f(x)dx \leq y_{\max}\int f(x)dx, \tag{33}$$

where $y(x)$ and $f(x)$ are positive in the range of integration. To scan the 20-Å wavelength interval in the neighborhood of 4000 Å, α changes by less than 3 min of arc. This corresponds to a change in $\cos(\alpha - \phi/2)$ of 0.02% and a change in $g(\lambda)$ of 1%, as estimated for our system by measuring the system response to the blackbody standard as a function of spectrometer setting. Thus,

$$\left|\frac{\int_0^\infty T(\lambda, \Lambda_0)d\lambda}{\int_0^\infty T(\lambda_0, \Lambda)d\lambda} - 1.00\right| \leq 0.01. \tag{34}$$

The second approximation requiring justification involves the value of the quantity

$$\frac{\int_0^\infty G(\lambda)\,\Delta I(\lambda)d\lambda}{A} = \frac{\int_0^\infty G(\lambda)\int_0^\infty [T(\lambda, \Lambda) - T(\lambda_0, \Lambda)]d\Lambda d\lambda}{\int_0^\infty G(\lambda)\,I(\lambda)d\lambda}. \tag{35}$$

Using Eq. (26), the Λ integral in the numerator may be written as

$$\begin{aligned}\Delta I(\lambda) &= \int_0^\infty [T(\lambda, \Lambda) - T(\lambda_0, \Lambda)]d\Lambda \\ &= \left\{\int_0^\infty\int_{-a}^{a} g(\lambda)D\left(x - \frac{f(\Lambda - \lambda)}{d\cos(\alpha - \phi/2)}\right) - g(\lambda_0)D\left(x - \frac{f(\Lambda - \lambda_0)}{d\cos(\alpha - \phi/2)}\right)\right\} d\Lambda dx \\ &= \int_{-a}^{a}\left[g(\lambda)\int_{u = u_1}^{-\infty} h(u, x)\,D(u)du - g(\lambda_0)\int_{u_0 = u_{01}}^{-\infty} h(u_0, x)D(u_0)du_0\right] dx,\end{aligned} \tag{36}$$

where

$$u = x - \{[f(\Lambda - \lambda)]/[d\cos(\alpha - \phi/2)]\},$$

$$h(u, x) = -\frac{d\cos(\alpha - \phi/2)}{f}\left[1 + \frac{x - u}{2f}\frac{\sin(\alpha - \phi/2)}{\cos(\phi/2)\cos\alpha}\right]^{-1} = \frac{d\Lambda}{du}, \tag{37}$$

and

$$u_1 = x + \{f\lambda/[d\cos(\alpha - \phi/2)]\},$$

with obvious extensions with $\lambda = \lambda_0$ in the integral over u_0.

The limits of integration in both the inner integrals of Eq. (36) are broad enough to include all values of u for which $D(u)$ has nonzero value. Thus, the integrals are not changed if we set $u_1 = u_{10} = +\infty$. Then the two integrals are identical. Noting that $I(\lambda)$ may be written in these terms as

$$I(\lambda) = g(\lambda)\int_0^{-\infty} h(u, x)D(u)du, \tag{38}$$

$\Delta I(\lambda)$ is given by

$$\Delta I(\lambda) = \{1 - [g(\lambda_0)/g(\lambda)]\}I(\lambda), \tag{39}$$

and Eq. (35) becomes

$$\frac{\int_0^\infty G(\lambda)\,\Delta I(\lambda)d\lambda}{A} = \frac{\int_0^\infty [1 - g(\lambda_0)/g(\lambda)]G(\lambda)I(\lambda)d\lambda}{\int_0^\infty G(\lambda)I(\lambda)d\lambda}. \tag{40}$$

Over the 20-A range of wavelengths covered by $G(\lambda)$, $g(\lambda)$ differs from $g(\lambda_0)$ by less than 0.5%. Thus, using the theorem of Eq. (33),

$$\left| \int_0^\infty G(\lambda)\Delta I(\lambda)d\lambda/A \right| \leq 0.005. \quad (41)$$

The third and final quantity requiring evaluation is

$$\frac{\int_0^\infty \Delta B(\lambda)\ T(\lambda,\ \Lambda_0)d\lambda}{H(\Lambda_0)} = \frac{\int_0^\infty \Delta B(\lambda)\ T(\lambda,\ \Lambda_0)d\lambda}{\int_0^\infty B(\lambda)\ T(\lambda,\ \Lambda_0)d\lambda}. \quad (42)$$

For a blackbody standard source the spectral intensity is given by Planck's law:

$$B(\lambda,\ T) = C_1\lambda^{-5}\ (e^{C_2/\lambda T} - 1)^{-1}. \quad (43)$$

For $T \approx 1000°\text{C}$ and $\lambda = 4000$ Å, $C_2/\lambda T \approx 28$, and Eq. (43) may be represented reasonably by the Wien radiation law:

$$B(\lambda,\ T) \approx C_1\lambda^{-5}e^{-C_2/\lambda T}. \quad (44)$$

For constant $T = 1000°\text{C}$, $\Delta\lambda = \pm 1$ Å [representing the wavelength width of $T(\lambda,\ \Lambda_0)$, or the instrument resolving power], and $\lambda_0 = 4000$ Å,

$$\Delta B(\lambda)/B(\lambda) = [C_2/\lambda T) - 5]\ \Delta\lambda/\lambda_0 \approx 23\Delta\lambda/\lambda_0 \approx \pm\ 0.006. \quad (45)$$

Using the theorem of Eq. (33) once again,

$$\left| \int_0^\infty \Delta B(\lambda)\ T(\lambda,\ \Lambda_0)d\lambda/H(\Lambda_0) \right| \leq 0.006. \quad (45)$$

This term is probably considerably smaller than this value. For example, if $T(\lambda,\ \Lambda_0)$ were symmetrical around $\lambda = \lambda_0$, the linear error term represented by Eq. (45) would give no contribution to the integral of Eq. (42), and the evaluation would have to be extended to the second term in the Taylor series expansion of $\Delta B(\lambda)$, which is quadratic in $\Delta\lambda$ and leads to an upper bound value of 10^{-5} for the quantity in Eq. (42). A better estimate might be to assume that $D(x - x_0)$ is symmetrical about $x = x_0$, in which case

$$\left| \frac{\int_0^\infty \Delta B(\lambda)\ T(\lambda,\ \Lambda_0)d\lambda}{H(\Lambda_0)} \right| \leq \left[\frac{\Delta B(\lambda)}{B(\lambda_0)}\right]_{\max} \left[\frac{\Delta g(\lambda)}{g(\lambda_0)}\right]_{\max} \approx (0.006)\ (0.01). \quad (47)$$

To this must be added the value resulting from the $(\Delta\lambda)^2$ term in the expansion of $\Delta B(\lambda)$, yielding a limit, for the case of symmetric $D(x - x_0)$, of about 10^{-4}.

Combining the results of Eqs. (34), (41), (46), and (47), Eq. (12) reduces, in this example, to

$$|[W - A\ B(\lambda_0)/H(\lambda_0)]/W| \leq 0.015 \text{ or } 0.02, \quad (48)$$

depending upon which estimate of the last error term is used.

Conclusion

The results of the previous section indicate that the commonly used method of calibrating spectroscopic measurements must be carefully examined for each combination of wavelength, spectroscopic analyzer, calibrating source and resolving power, to mention the most obvious of the variables involved. Such justification must show that the values of the error integrals of Eq. (12) are appropriately bounded. Unless proper precautions are taken and appropriate justifications provided, all absolute and relative spectral irradiance measurements are subject to unknown systematic errors, and the ultimate precision attainable by such measurements is severely limited.

The most serious error arises from changes in detector sensitivity and optical transmission of the spectrometer over the wavelength interval included in the spectral feature. If this interval is small, as is the case for a sharp spectral line, the calibration procedure can be justified to within approximately 1%. If the interval is large, as for an extended molecular band system, the problem is more difficult. In this case it may be necessary, for example, to calibrate the instrument output point by point before measuring the area under the spectral feature.

A second source of error is the change in the emission of the blackbody standard over a wavelength interval comparable to the resolving power of the instrument. This will contribute only a small error to measurements made with high resolving power, but may contribute significantly if, for example, the resolving power of the instrument is compromised to achieve greater sensitivity.

References

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2. James E. Stewart, Appl. Opt. **4**, 609 (1965).