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Error Analysis of the Transmittance Ratio Stray Radiant Energy Test Method in Double-beam Ratio Recording Spectrophotometers

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The photometric error contributions which the relative errors in determining both the cell pathlength ratio and the transmittance ratio minimum make towards the relative error in determining the relative stray radiant energy (SRE) levels in a ratio recording double-beam spectrophotometer were investigated, thus enabling optimum experimental conditions for SRE determination to be pre-selected.

Keywords: *Transmittance ratio; stray radiant energy; error analysis; ratio recording spectrophotometer*

An experimental method for determining an instrumental specification is of uncertain merit unless it has been fully error analysed. The Fleming[1,2] and Mielenz *et al.*[3] transmittance ratio spectrophotometric methods for determining the relative stray radiant energy (SRE) level, *s*, in ratio recording double-beam spectrophotometers involve photometric measurements which are subject to error (*cf.*, Gridgeman).[4] Inspection of the equation

$$s = \frac{(\alpha-1)(\rho/\alpha)^{\alpha/(\alpha-1)}}{1-\rho} = \frac{(\alpha-1)\tau^{\alpha}}{1-\alpha\tau^{\alpha-1}} \qquad (1)$$

which relates *s* to the transmittance ratio minimum, ρ, to the reference beam's monochromatic transmittance value, τ, where the transmittance ratio is a minimum, and to the cell pathlength ratio, α, suggests that there is a connection between the photometric error and the error in determining *s*. Remember that $\rho = \alpha\tau^{\alpha-1}$ and that α, which Burgess and Knowles[5] implied may be determined photometrically to a precision of 4%, also contributes to the error in determining the SRE level.

This paper investigates the photometric error contributions which the relative errors in determining both the cell pathlength ratio, $\Delta\alpha/\alpha$, and the transmittance ratio minimum, $\Delta\rho/\rho$, make towards the relative error in determining the relative SRE levels, $\Delta s/s$, in a double-beam spectrophotometer, thus enabling optimum experimental conditions to be pre-selected when using the transmittance ratio SRE determination method.

Formulation of Experimental Quantities

The dependence of the relative error in determining *s* on the relative errors in ρ and α may be derived from eqn. (1) via the equation

$$\ln s = \ln(\alpha - 1) + [\alpha/(\alpha - 1)]\ln(\rho/\alpha) - \ln(1 - \rho) \qquad (2)$$

Since $\rho = \alpha\tau^{\alpha-1}$, eqn. (2) becomes

$$\ln s = \ln(\alpha - 1) + \alpha\ln\tau - \ln(1 - \alpha\tau^{\alpha-1}) \qquad (3)$$

Differentiating eqn. (3) gives

$$\Delta s/s = A[B(\Delta\alpha/\alpha) + C(\Delta\tau/\tau)] \qquad (4)$$

where

$$A = [(\alpha - 1)(\alpha^{-1} - \tau^{\alpha-1})]^{-1}$$

$$B = 1 + (\alpha - 1)\ln\tau - \tau^{\alpha-1}$$

$$C = (\alpha - 1)(1 - \tau^{\alpha-1})$$

Skoog and Leary[6] gave the photometric error in a double-beam ratio recording spectrophotometer, ΔT, as $k(T + T^2)^{1/2}$, where *k* is a constant for a given spectrophotometer. The Perkin-Elmer 551S spectrophotometer specification gives $\Delta T = 0.0012$ at $T = 0.1$, yielding $k = 0.0036$. Therefore, the relative error in τ is given by

$$\Delta\tau/\tau = 0.0036(1 + \tau^{-1})^{1/2} \qquad (5)$$

The relative error function in eqn. (5) has values in the range $0.012 < \Delta\tau/\tau < 0.114$ for $0.1 > \tau > 0.001$.

If the pathlength ratio is determined spectrophotometrically,[5] then its relative error, $\Delta\alpha/\alpha$, is dependent on the photometric error, ΔT, for the particular spectrophotometer employed. It may be shown for the Perkin-Elmer 551S instrument that

$$\Delta\alpha/\alpha = (0.0036/\ln T_r)[\alpha^{-2}(1 + T_r^{-\alpha})^2 + (1 + T_r^{-1})^2]^{1/2} \qquad (6)$$

where T_r is the monochromatic transmittance of a dilute sample placed in the reference cell so as to compare its thickness with that of the sample cell and hence to calculate α. The relative error function in eqn. (6) has values in the range $0.049 > \Delta\alpha/\alpha > 0.040$ for $1.1 < \alpha < 10$ and $T_r = 0.8$. Note that the dilute solution in question is used solely to establish spectrophotometrically the experimental cell pathlength ratio rather than relying on the nominal pathlengths marked on the cells.

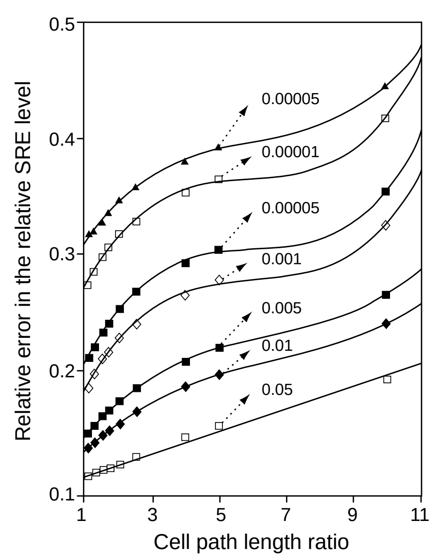

Fig. 1 Relative error in the relative stray radiant energy level, $\Delta s/s$, plotted against the cell pathlength ratio, α, for seven distinct relative stray radiant energy levels, s = 0.05, 0.01, 0.005, 0.001, 0.0005, 0.0001 and 0.000 05.

The root mean square relative error, $(\Delta s/s)_{rms}$, is given by

$$(\Delta s/s)_{rms} = A[B^2 (\Delta\alpha/\alpha)^2 + C(\Delta\tau/\tau)^2]^{1/2} \quad (7)$$

Analysis and Conclusion

Eqn. (7) was solved for relative SRE levels in the range $0.05 > s > 0.00005$, for cell pathlength ratios in the range $1.1 < \alpha < 10$ and for $T_r = 0.8$. Fig. 1 shows the relative error function as set out in eqn. (7), $(\Delta s/\Delta)_{rms}$, plotted against the cell pathlength ratio, α, for seven distinct relative SRE levels.

The relative error function increases with increasing cell pathlength ratio for a given relative SRE level, and increases with decreasing relative SRE levels for a given cell pathlength ratio. Sample cells come in standard sizes of 1, 2, 5, 10, 20, 50 and 100 mm. Considering the dependence of the error function on the cell pathlength ratio, we recommend $\alpha = 2$ as it may be selected in four independent ways from the above cell size set and it also makes eqn. (1) easy to calculate since $\rho = 2\tau$ and $s = \rho^2/4(1 - \rho) = \tau^2/(1 - 2\tau)$.

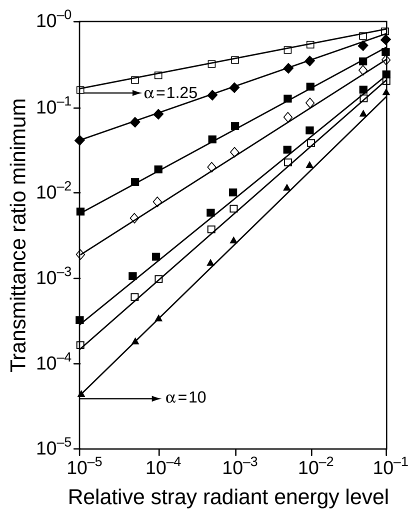

Fig. 2 Transmittance ratio minimum *versus* relative SRE level plotted on log–log axes for $\alpha = 1.25$, 1.5, 2.0, 2.5, 4, 5 and 10.

Burgess[7] has shown graphically the dependence of the transmittance ratio minimum on the reference beam's monochromatic absorbance ($= -\log_{10}\tau$) in the relative SRE range $0.1 > s > 0.00005$ and for $\alpha = 1.25$. Fig. 2 shows the corresponding graphs for $\alpha = 1.25$, 1.5, 2, 2.5, 4, 5 and 10, which may be utilized to calculate readily the relative SRE level once the transmittance ratio minimum has been determined.

An *a priori* knowledge of the approximate relative SRE level in a spectrophotometer, *e.g.*, gleaned from its specification sheet, will suggest the monochromatic absorbances of a narrow range of reference beam solutions which need to be prepared for a given α so as to make possible a rapid experimental determination of ρ. Fig. 2 allows the rapid calculation of the reference beam's monochromatic absorbance from the transmittance ratio minimum at any given relative SRE level and α value. Spectrophotometers are usually operated in the absorbance mode rather than in the transmittance mode and therefore differential absorbance rather than transmittance ratio is observed in this application. Differential absorbance is a slowly varying function of the monochromatic reference absorbance at and near the differential absorbance maxima, *i.e.*, it is 'flat-topped.'

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