Range and Error of Densitometers for Emission Spectroscopy*

MASTER

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Abstract

The errors in measurement of spectral energy, due to scale errors of the transmission type densitometer, have been evaluated. It is shown that the range of measurement is a direct function of the permissible errors.

Present day densitometers are arranged to measure the proportion of the incident light that is transmitted by the photographic image of the spectral line. The readout is generally a galvanometer with a linear scale or a recorder which is also linear, although occasionally the strip chart may be printed in logarithmic units. A peculiarity of the transmission densitometer is that the measurement is inverse to usual electrical instruments in that the smaller the excursion of the needle the larger the quantity measured.

It must be apparent, therefore, that the distribution of errors will not be a simple function of scale reading; in fact, there will be two regions of high error -- at the low end of the scale because of the high scale error, as in other indicating instruments, and also at the high end because of the

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small base of measurement. The general causes of these errors are instability of the electronic circuit, which gives rise to erratic shifts of the zero and 100% settings, and to the non-linearity of the response. There are additional errors of densitometry, but these are due to failings of the emulsion and its processing, and will not be considered here.

The range of measurement is tied in directly with the extent and distribution of the errors. Although this range is theoretically infinite in a zero to 100% scale, in practice a limit must be set on the error to be tolerated, and this constrains the scale and therefore the range. The latter may thus be defined as the ratio of highest to lowest reading which do not exceed an arbitrarily set error. The precision and range bear an inverse relationship -- the higher the precision the shorter the range.

One additional factor must be mentioned. The scale readings are just that, merely parameters of the quantity of real interest, which is the spectral energy causing the line in the first place. Error and range must therefore be converted to light energy units (by means of the characteristic curve) to be practically useful.

Of course, the above argument is well understood in a qualitative sense by workers in the field, but quantitative applications are conspicuously lacking. For example, in a survey I undertook of the ASTM book of recommended procedures (1), of some hundred emission methods there described, 27 specify a restriction in the densitometer range, but there appears to be no consistency among the various authors. Directions for the high end of the scale varied from 80 to 97 percent transmittance, and for the low end the variation was from 3 to 20 percent transmittance. Obviously, these figures were arrived at by guessing, for there is no mention of permissible error, and indeed no

such figure can be given in terms of scale range, because this depends on the design, adjustment and mode of use of the individual instruments. A similar survey of the published literature shows the same state of affairs.

It is not difficult to develop an expression for the densitometer error function, which would make guessing of the permissible range unnecessary. Gridgeman (2) has done this for spectrophotometers, and his general procedure can be followed for the present problem. I begin by assuming that the emulsion characteristic is known, and that the various scale errors have been determined and are also known. Denoting these latter by a , b , c ... n , the error of a transmittance reading σ_T will be

$$\sigma_T = \pm \sqrt{a^2 + b^2 + c^2 \dots n^2}$$

and the resulting error, σ_E , in energy E will be

$$\sigma_E = \frac{dE}{dT} \sigma_T$$

where T is the transmittance. For the coefficient of variation F we may write

$$F = \frac{\sigma_E}{E} = \pm \frac{dE}{dT} \frac{\sqrt{a^2 + b^2 + c^2 \dots n^2}}{E} \quad (1)$$

This is the general expression sought. It remains now to evaluate it in terms of the photographic characteristic. This cannot be done easily because the characteristic cannot be represented by a simple analytical equation. However, one mode of attack is to consider the characteristic, when plotted in D -- $\log E$ co-ordinates, as being made up of two joined curves -- a straight portion at higher densities and a curved portion at lower densities, with the point of juncture at approximately 0.5 on the density axis. This is the usual

experience for the slow, undyed emulsions used in the ultraviolet by spectrochemists.

Considering first the straight portion, this follows the function

$$D = \gamma \log E$$

where D is photographic density and γ the slope or contrast. By definition,

$$D = \log \frac{1}{T} = -\log T$$

$$\text{and } \gamma \log E = -\log T$$

$$\text{or } E = T^{-1/\gamma}$$

Differentiating, reducing and substituting in (1) we obtain

$$F = \frac{\sqrt{a^2 + b^2 + c^2 \dots n^2}}{\gamma T}$$

which is the expression for the low transmittance end of the characteristic.

For the toe portion the simplest procedure is to plot the characteristic in T,E coordinates and then fit a second order equation to the resulting curve.

The differential, if the equation is in the form $E = AT^2 + BT + C$, will be $dE/dT = 2AT + B$ and the coefficient of variation for the toe portion will be

$$F = \frac{2AT + B}{E} \sigma_T$$

Example. As an example of how these equations may be applied to practical problems, we will take the error data for the densitometer in the Chemistry Department at Brookhaven National Laboratory. This is a modern, double beam, photomultiplier instrument in good adjustment and used in a fashion typical, it is hoped, of good practice. The transmittance scale is divided into 500 parts, and can be read unambiguously to one-half of one of these

divisions, or 0.002. At the 100% end the instability is 5 divisions or 0.01, but this error directly diminishes with the scale reading and so is equal to 0.01 T. It is assumed that the galvanometer response is linear and introduces no error on that account. Surely the manufacturer has no cause to be ashamed of this performance, and, in fact, it is quite close to catalog specifications.

It is interesting to apply these densitometer errors to a very commonly used emulsion, Eastman's Spectrum Analysis #1. A reliable source for the characteristic of this emulsion is found in a publication of Sherman (3), who presents the coordinates, $\log E$ versus density, in tabular form for a gamma of unity and for a wavelength of 3000 Å, although he shows in the same chapter that the shape is independent of wavelength.

Following the procedure outlined above, the graph of the error function was worked out and the result is shown in Figure 1, which is the expected U-shaped curve (as modified by the emulsion characteristic) in terms of spectral energy units and percent transmittance. Note that the abscissa scale changes at 10% in order to show the relationship more clearly, although with a uniform scale the curve would have been more symmetrical. The curve goes through an optimum of about 1% at a transmittance of approximately 30%, a necessary condition as pointed out by Twyman and Lothian (4); this then is the best that could be done under the assumed conditions, and for scale readings away from this level the error will be larger. This should be compared with the statement in the standard text by Harrison, Lord and Loofbourow (5) "Instrumental errors can readily be kept below 0.5% for the direct reading type (of densitometer) and below 0.2% for the null type."

The curve of Figure 1 tells us nothing of the range restrictions. For this we must decide on an arbitrary limiting error and see how it falls with

respect to the H & D curve. This is shown in Figure 2, which is a plot of the characteristic from Sherman's data in terms of log transmittance and energy, with the range scaled for 2 and 3% maximum error. The usable scale range for a 2% error is from 8.5 to 63% transmittance and for 3% the range increases to 6.3-75%; in terms of energy these are ranges of 12 and 27, respectively. In terms of the usual internal standard procedure, if for instance it is decided that the maximum instrumental error shall be no greater than 2%, the exposure must be so controlled that the internal standard line, in order to occupy a central position, have a value of 3.5 arbitrary units, then lines of the unknown of 1 to 12 units can be used. For a 3% maximum error the spread will be somewhat greater, but no markedly so. It can be appreciated that the exposure control is critical and the concentrational range for a particular line is small. This raises difficulties particularly for arc exposures. The temptation to use too weak or too dense lines must be strong and frequent, especially when the consequences are little understood.

Literature Cited

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Figure Captions

Fig. 1. Error Function Under the Assumed Conditions

Fig. 2. Plot of H & D Curve with Range of Measurement for the Errors Shown

FIGURE 1

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FIGURE 2