

Phosphorescence Mechanisms. III. Method of Analysis

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The method of deconvolution is discussed for the case in which phosphorescence is distributed between a number of concurrent components with different rate constants. The resolution of the method is deduced quantitatively from the known rms difference of the apparatus.

IN Part I a number of different composite arrangements of individual processes were envisaged as possible mechanisms of phosphorescence, and qualitative methods of recognizing these mechanisms were discussed. Almost all the phosphorograms so far recorded are recognizable as arising from groups of concurrent processes, and so analysis consists of discovering the best decay rate spectrum for each phosphorogram. The analysis technique has been developed empirically, and though it appears to form a basis for more complicated mechanisms, the development of a technique for any other mechanism will have to await sufficient suitable data.

RESOLUTION

Any one component (p, α) of the decay rate spectrum cannot be distinguished from two components each of about half the weight and with slightly separated rate constants if the phosphorograms in the two cases do not differ by more than their rms difference. This error is known from the test data on the phosphorometer given in Part II, and so a theorem on the resolution of the decay rate spectrum can be deduced. It is convenient to introduce two new functions to the notation of Part I to simplify the logarithmic representation of frequency and rate constant.

Let

$$m(f) = 10 \log_{10} f, \quad (1)$$

and

$$n(\alpha) = 10 \log_{10}(\alpha/2\pi); \quad (2)$$

then the equation of the elementary phosphorogram becomes

$$\chi(m, n) = (1 + 10^{(m-n)/5})^{-1}. \quad (3)$$

By the further substitution

$$y = (m - n)/5 \log_{10} e, \quad (4)$$

(3) becomes

$$\chi(y) = (1 + e^y)^{-1}. \quad (5)$$

The resolution can now be defined precisely as the separation Δn of two concurrent components of equal weight $\frac{1}{2}p$ whose phosphorogram differs by just the known rms difference $\Delta\chi$ from that of a single component of weight p at their center. In terms of the rate constants themselves this is equivalent to defining a

minimum resolution ratio ($\Delta n > 0$)

$$\alpha(n + \Delta n)/\alpha(n) = \text{antilog}_{10}(\Delta n/10). \quad (6)$$

The definition of resolution may be written analytically as

$$\Delta\chi = p\chi(y) - \frac{1}{2}p[\chi(y + \delta) + \chi(y - \delta)], \quad (7)$$

where $\delta = \Delta n/(10 \log_{10} e)$. With the aid of (5), Eq. (7) becomes

$$\begin{aligned} \Delta\chi/p &= [(1 - \cosh \delta) \sinh y] / [2(\cosh y + \cosh \delta)(1 + \cosh y)], \\ &\text{and is reduced to} \end{aligned}$$

$$\Delta\chi/p = -\delta^2 (\sinh y) / [4(1 + \cosh y)^2] \quad (8)$$

for small values of δ . The values of y for which this difference is greatest are given by the equation

$$\cosh y = 2.$$

This occurs at a displacement of nearly 3 units of m on either side of the mean rate constant.

At these values of y ,

$$\Delta\chi/p = \pm 0.0481\delta^2,$$

and in terms of Δn

$$\Delta\chi/p = \pm (\Delta n)^2/392. \quad (9)$$

Table I shows this relation in numerical form after inserting the rms difference $\Delta\chi = 0.002$ as deduced in Part II. The tabulation is for exact values of the log scale resolution, and the corresponding ratios of rate constants from relation (6) is also included.

Three inferences can be drawn from the resolution equation (9).

1. The phosphorometer cannot effectively handle components accounting for less than a few percent of the total emitted radiation.

TABLE I. Resolution of phosphorometer related to weight of component.

| Resolution on log scale, Δn | 1 | 1.5 | 2 | 3 | 4 |
|--|------|------|------|------|------|
| Resolution ratio | 1.26 | 1.41 | 1.58 | 2.00 | 2.51 |
| Weight of component, p | 0.78 | 0.35 | 0.20 | 0.09 | 0.05 |

2. Further efforts to increase the precision of the instrument are unlikely to be worth the expenditure.

3. Because the best resolution for a major component is about $\Delta n = 1$, it is appropriate both to make measurements and to attempt synthesis at intervals of frequency given by $\Delta m = 1$.

SYNTHESIS METHOD

The practicability of a synthesis method consists in being able to compute a trial synthesis quickly, in obtaining a simple comparison with the experimental data, and in being able to use the difference between the two to indicate a better choice of trial parameters. Comparisons of experimental and synthesized phosphorograms were made initially by tracing and superposition. It promotes a useful understanding of the function, but in the end does not repay the time spent in accurate plotting of trial syntheses.

In seeking a numerical method it is evident that the experimental data will have to be converted to a form more suitable for numerical comparison. The instrumental limitations restrict m between the bounds

$$5 \leq m \leq 45.$$

It is convenient to make measurements at half odd-integral values of m so as to avoid the power frequency (50 cps) and its multiples, but it is uneconomical of time to adjust the oscillator to correspond precisely with half odd-integral values of m . Accordingly a numerical method cannot be used directly, and for the early results a graphical method of interpolation and smoothing was used to obtain a derived set of experimental data (χ, m), where m assumes exact integral values.

It is not necessary to have access to a continuous range of choice of rate constant in order to obtain sufficiently accurate coverage by synthetic phosphorograms. Except for components of weight nearly equal to unity, a discrete range at intervals $\Delta n = 0.05$ is adequate; and for weighting factors of the order $p = 0.1$, the intervals can be increased to $\Delta n = 0.2$. To appreciate the synthesis process it is convenient to suppose the integral values of m (5 to 45) to be arranged vertically, and the corresponding derived experimental χ 's written alongside each. The values of the elementary function (3) are tabulated at integral values of m onto vertical cardboard strips with the entries at the same spacing. Tabulations on different strips are made for each of the fractional values of n from 0 through to 0.95. The whole-number part of n can be accommodated by setting the strip to correspond with the desired value of m (5 to 45), and the fractional part by choosing the appropriate strip. It is convenient also to have these tabulations made for a range of different weights, p , although this considerably increases the initial labor. However once equipped with such a matrix of strips, a synthesis may be set out by choosing the desired weights, p , and the

fractional parts of n for each trial process and setting them side by side in the appropriate vertical positions for the whole-number parts of n . The synthetic phosphorogram is then rapidly computed by summing the entries on all the strips horizontally at each value of m in turn. The differences between experimental and synthetic phosphorograms can then be found by subtraction for each value of m .

After entering the derived experimental values of χ at each integral value of m , it is helpful to compute the first differences in χ and to check that these are less than those for a strip of weight unity. The value of m corresponding to the largest first differences will be approximately the value of n for the component of largest weight. Submaxima of first differences are likely also to point to the positions of other components but the converse is not true unless the components are well separated. It is convenient to begin the synthesis by assessing the amount of weight that should be allotted to components outside the range from the values of χ at the extremes, and then to allot all the remaining weight to a single process in the range at the maximum of the first differences. The fitting error between this trial phosphorogram and the derived experimental one gives a good indication of where additional components will have to be placed.

As with other deconvolution problems such as the determination of crystal structures from diffraction data, the choice of the trial parameters and the adroitness of the refinement procedure depend heavily upon the experience of the worker. The convolution strips make the computation of each trial phosphorogram a convenient though still tedious process. Although the deconvolution is only one-dimensional there is no *a priori* knowledge of how many components are involved. The guiding principle must therefore be to invoke as few components as possible, and to increase the number only after being satisfied that there is otherwise no possible synthesis. Refinement is continued until the rms difference between the derived experimental values and the synthesized values is about equal to the rms difference $\Delta\chi = 0.002$.

A systematic method of synthesis makes it most unlikely that the correct decay rate spectrum is any simpler than that proposed in the refined synthesis. Once the refinement is complete, the tolerance on the parameters is very close, particularly for processes of major weight.

The problem of uniqueness of the refined decay rate spectrum at present defies rigorous treatment, apart from certain evident corollaries of the resolution equation (9). This situation is not unusual in analytical techniques which involve repeated trial synthesis. Confidence in the results is increased when they are shown to be compatible with related measurements. As yet no such measurements are known to the author.