USE OF THE WRONSKIAN DETERMINANT IN THE STUDY OF MULTICOMPONENT SYSTEMS

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SUMMARY
The use of Wronskian determinants in the study of multicomponent systems is proposed. The general theory is presented and applied to the spectrophotometric determination of the number of linearly independent components—absorbers. A detailed study of a two-component system is presented and analysed. Numerical methods for smoothing and differentiation of digitized spectra via cubic splines are used.

KEY WORDS
Wronskian determinant Multicomponent systems Derivative spectroscopy
Spline functions

INTRODUCTION
The problem of studying complex multicomponent systems without separation of the components is well known. Generally, the situation arises whenever interactions between components are essential in determining the function of the system, notably in biochemical systems and in catalysis. In cases such as these, the ultimate aim is to deduce the role of each of the components as well as the interactions between them by measuring collective properties with non-destructive techniques.

The problem was formulated several years ago, but it is instructive to state it once more in simple and clear terms, using spectrophotometric measurements as an example. If one measurement is taken in a solution containing two unknown solutes, an equation is obtained with four unknowns:

\[ A_1 = \varepsilon_1(\lambda_1)c_1 + \varepsilon_2(\lambda_1)c_2 \]  

If another measurement is taken, at another wavelength, one equation is added but also two unknowns, i.e. the absorptivities at the new wavelength, and so on. In general the number of unknowns is \( n^*(n+1) \), where \( n^* \) is the number of absorbing components and \( n \) is the number of wavelengths. Thus there is no way to solve the problem by merely taking more measurements. Even with an infinite number of measurements, e.g. by taking the whole
The ratio of the number of unknowns over the number of equations equals \( n^* (\geq 1) \).

In the discussion above the concentrations were considered constant and the wavelength was the independent variable.

Alternatively the wavelength can be fixed and the concentrations varied, e.g. as in a reacting system measured at various times. In this case too the number of unknowns is \( n^* (n+1) \), \( n^* \) being the number of absorbing species and \( n \) the number of measurements. Again the number of unknowns exceeds the number of equations. It is also obvious that the situation does not change even if we consider simultaneously the wavelength and the time as independent variables. In fact, owing to the nature of these particular measurements, the variables are already separated, and in a mathematical sense there seems to be no advantage in mixing them up, since normally we are trying to do the opposite in order to facilitate the solution.

The inevitable conclusion is that we need more equations: relations between the absorptivities \( \epsilon (\lambda) \) or between the concentrations \( c(t) \). The absorptivities of one component may be related to each other functionally, e.g. through a Gaussian. In that case the number of unknowns is reduced to \( 3n^* \), three being the number of parameters in the Gaussian function, which are the same for all \( \epsilon s \) of a given component. The problem is then readily solved by measuring at \( 3n^* \) wavelengths without introducing new unknowns every time the wavelength changes.

A similar reduction may be achieved if we assume a functional dependence among the concentrations of given components, e.g. based on an assumed mechanism and its kinetics.\(^5\) The concentrations may also be related through the stoichiometry.

The disadvantage of this approach is that it rests on rather unsubstantiated assumptions. A Gaussian function, for example, is at most just a reasonable approximation of the actual spectra, and the kinetics are, as a rule, speculative.

An easier problem is to determine the number of linearly independent absorbers, which is usually equal to the number of absorbers. Linear dependence between components is rather uncommon.

If two components are related through the equilibrium
\[
X \rightleftharpoons K Y
\]
there is a linear relation between the concentrations
\[
c_X = K c_Y
\]
However, in an equilibrium of the type
\[
X + Y \rightleftharpoons \frac{K'}{Z}
\]
the relation between the concentrations is not linear. Also, in a reacting system
\[
X \rightarrow K Y
\]
the concentrations are related through the stoichiometry, which again is not linear.

The mathematical techniques found in the literature for determining the number of linearly independent absorbers in multicomponent chemical systems are based on the determination of the rank of the matrix of the experimentally determined absorbances. However, the
USE OF WRONSKIAN DETERMINANT

Table 1. The Gaussian and its derivatives up to the fourth

\[
\begin{align*}
\varepsilon(\lambda) &= \varepsilon_0 \exp\{-4 \ln 2 \left(\frac{\lambda - \lambda_0}{w}\right)^2\} \\
d\varepsilon(\lambda)/d\lambda &= -\varepsilon(\lambda) [8 \ln 2(\lambda - \lambda_0)/w^2] \\
d^2\varepsilon(\lambda)/d\lambda^2 &= \varepsilon(\lambda) [8 (\ln 2)^2(\lambda - \lambda_0)^2/w^2 - 8 \ln 2(\lambda - \lambda_0)/w^2] \\
d^3\varepsilon(\lambda)/d\lambda^3 &= \varepsilon(\lambda) \left[3(\ln 2)^2(\lambda - \lambda_0)^2/w^2 + (8 \ln 2)^2(\lambda - \lambda_0)^4/w^4\right] \\
d^4\varepsilon(\lambda)/d\lambda^4 &= \varepsilon(\lambda) \left[(8 \ln 2)^2(\lambda - \lambda_0)^4/w^4\right]
\end{align*}
\]

experimental error is propagated during the calculations\(^4\) and the presence of minor components is difficult to confirm.

In this paper we introduce the Wronskian determinant, to the best of our knowledge for the first time in the chemical literature. This determinant includes derivatives of the absorbance curve, which are much more sensitive than the absorbance itself to the presence of minor components. Considering, for example, a Gaussian band, we see (Table 1) that higher derivatives are inversely dependent on higher powers of the half-width. Minor components can be easily overlooked if we deal with absorbances, but if they have small half-width relative to a major component, the contribution to higher-order derivatives is large, measurable and will be reflected in the value of the Wronskian.

Another advantage of the Wronskian is its generality (see below), namely the fact that it can be applied not only to spectrophotometric data but to any measurements of a collective property of the system, provided that the contribution of each of the components to this property is characteristic and dependent on some variable. Obviously, components with identical contributions cannot be distinguished.

The use of the Wronskian in the determination of the number of components by performing measurements on mixtures is particularly useful in cases where the contributions of the components overlap. In spectroscopy, for example, if the bands are well resolved, the determination of the number of components or even their identification is rather trivial, and it is only when the components have overlapping contributions at a range of values of the wavelength that this task becomes difficult.

The use of the Wronskian is now possible because of the development in recent years of derivative spectroscopy.\(^6\)\(^-\)\(^11\)

THE WRONSKIAN

Let \(u_1(x), u_2(x), \ldots, u_n(x)\) be functions which are defined and continuous within the same interval \((a, b)\) and have derivatives \(u_1^{(k)}(x), u_2^{(k)}(x), \ldots, u_n^{(k)}(x), k = 1, 2, \ldots, (n - 1)\), which are continuous functions in this interval. The determinant

\[
W(x) = \begin{vmatrix}
u(1) & u_2^{(1)} & \ldots & u_n^{(1)} \\
u(1) & u_2^{(1)} & \ldots & u_n^{(1)} \\
\vdots & \vdots & \ddots & \vdots \\
u(n-1) & u_2^{(n-1)} & \ldots & u_n^{(n-1)}
\end{vmatrix}
\]

is continuous for every \(x\) within the interval \((a, b)\) and is called 'the Wronskian determinant' (or simply the Wronskian) of the functions \(u_1, u_2, \ldots, u_n\). In this determinant \(u_n^{(1)}\) denotes the first derivative with respect to \(x\), namely \(du_n/dx\), \(u_n^{(2)}\) the second derivative \(d^2u_n/dx^2\), and so on.
The following abbreviated form for the Wronskian is often used
\[ W(x) = \begin{vmatrix} u_1, u_2^{(1)}, u_3^{(2)}, \ldots, u_n^{(n-1)} \end{vmatrix} \]
in which only the diagonal elements are written. This, and analogous abbreviations for the other determinants, will also be used in this paper, and a similar abbreviation for matrices, but with square brackets instead of vertical lines.

The chief property of the Wronskian is that it vanishes for every \( x \) within the interval \((a, b)\) if \( u_1, u_2, \ldots, u_n \) are linearly dependent, e.g. if
\[ \alpha_1 u_1 + \alpha_2 u_2 + \cdots + \alpha_n u_n = 0 \quad \text{(not all } \alpha s \text{ zero)} \]
then
\[ W_n = 0 \]
If \( u_1, u_2, \ldots, u_n \) are linearly independent, e.g. if
\[ \alpha_1 u_1 + \alpha_2 u_2 + \cdots + \alpha_n u_n \neq 0 \]
then
\[ W_n \neq 0 \]
The formulation so far is perfectly general. Each function \( u_n(x) \) is a property of a mixture containing \( n \) components, each component having a characteristic contribution to this property.

If we prepare \( n \) linearly independent compositions of \( n \) linearly independent components, and make \( n \) measurements \( u_1(x), u_2(x), \ldots, u_n(x) \), the values of these measurements are also linearly independent (Appendix). If the \( n \) values of the \( n \) measurements are linearly independent, then the number of linearly independent components is also \( n \).

A special case is to measure light absorbance. Beer–Lambert’s law is usually expressed in the form (assuming unit light path length)
\[ A_j(\lambda) = \sum_{i=1}^{n} e_i(\lambda)c_{ij} \]  
(2)
where \( A_j(\lambda) \) is the spectrum of the \( j \)th composition and \( c_{ij} \) is the concentration of the \( i \)th component in the \( j \)th composition.

The Wronskian of the absorbances \( A_1, A_2, \ldots, A_n \) is
\[ W_n(\lambda) = \begin{vmatrix} A_1, A_2^{(1)}, \ldots, A_n^{(n-1)} \end{vmatrix} \]
If \( W_n(\lambda) \neq 0 \), then the system consists of \( n \) linearly independent components and the \( n \) compositions chosen are linearly independent. Consequently the Wronskian of \( A_1, A_2, \ldots, A_n \) plus the absorbance \( A \) of any other composition must vanish
\[ W_{n+1} = \begin{vmatrix} A_1, A_2^{(1)}, \ldots, A_n^{(n-1)} A^{(n)} \end{vmatrix} = \begin{vmatrix} A_1 & A_2 & \cdots & A_n & A \\ A_1^{(1)} & A_2^{(1)} & \cdots & A_n^{(1)} & A^{(1)} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ A_1^{(n)} & A_2^{(n)} & \cdots & A_n^{(n)} & A^{(n)} \end{vmatrix} = 0 \]

Expanding by the elements of the last column, we obtain
\[ | A_1, A_2^{(1)}, \ldots, A_n^{(n-1)} | A^{(n)} - | A_1, A_2^{(1)}, \ldots, A_n^{(n-2)} A_n^{(n)} | A^{(n-1)} + \cdots + (-1)^n | A_1^{(1)}, A_2^{(2)}, \ldots, A_n^{(n)} | A = 0 \]  
(3)
The determinant coefficients in equation (3) may be calculated from experimental data and contain all the spectral information of the multicomponent system. All the spectra of all possible compositions of the given absorbers are solutions of this differential equation, or put differently, the solutions of equation (3) span the n-dimensional space of all possible measurements.

The general solution of the homogeneous linear differential equation (3), with variable coefficients, is a linear combination of n linearly independent terms

\[ A(\lambda) = b_1 A_1(\lambda) + b_2 A_2(\lambda) + \cdots + b_n A_n(\lambda) \]  

What equation (4) essentially means is that the spectra of any n linearly independent compositions of n components can be used as a base in order to describe the spectrum of the \((n+1)\)th composition. Beer–Lambert's law is a special case of this in which \(A_1, A_2, \ldots, A_n\) are identified as the spectra of each of the components, e.g. the \(A_s\) are identified as the absorptivities of the separate components.

The determinant coefficient of kth order may be written

\[ | A_{11}, \ldots, A_{k-1}, A_{k+1}, \ldots, A_{n(n)} | = | \varepsilon_1, \ldots, \varepsilon_k^{(k-1)}, \varepsilon_{k+1}^{(k+1)}, \ldots, \varepsilon_n^{(n)} | D(c) | \]

Consequently, equation (3) becomes

\[ | \varepsilon_1, \ldots, \varepsilon_2^{(1)}, \ldots, \varepsilon_n^{(n-1)} | || D(c) || A^{(n)} - | \varepsilon_1, \varepsilon_2^{(1)}, \ldots, \varepsilon_{n-1}^{(n-2)}, \varepsilon_n^{(n)} | || D(c) || A^{(n-1)} + \cdots + (-1)^n | \varepsilon_1^{(1)}, \varepsilon_2^{(2)}, \ldots, \varepsilon_n^{(n)} | || D(c) || A = 0 \]

However, we may choose arbitrary mixtures for which \(| D(c) | \neq 0\). Hence

\[ | \varepsilon_1, \varepsilon_2^{(1)}, \ldots, \varepsilon_n^{(n-1)} | A^{(n)} - | \varepsilon_1, \varepsilon_2^{(2)}, \ldots, \varepsilon_{n-2}^{(n-2)}, \varepsilon_n^{(n)} | A^{(n-1)} + \cdots + (-1)^n | \varepsilon_1^{(1)}, \varepsilon_2^{(2)}, \ldots, \varepsilon_n^{(n)} | A = 0 \]

APPLICATION

The theoretical methods described were applied to a system with two linearly independent absorbers, namely chloroform solutions of tris(acetylacetonato)chromium(III), \(\text{Cr(acac)}_3\), and tris(acetylacetonato)cobalt(III), \(\text{Co(acac)}_3\).

This particular system was chosen because (i) the spectra of the absorbing species may be well simulated by simple functions (asymmetric Gaussians) over a large range of wavelengths, (ii) the solutes are very stable and (iii) it has been reported that these solutions conform approximately to Hildebrand’s criteria for regular solutions.\(^{14}\)

\(\text{Cr(acac)}_3\), \(\text{Co(acac)}_3\) and chloroform (spectroscopic quality, alcohol-free and freshly distilled) were all purchased from Fluka.

Absorption spectra of the solutions were recorded in the 460–750 nm region in 1 cm quartz cells. These spectra have been assigned by Barnum.\(^{15}\)

The measurements were made with a Cary 17D spectrophotometer connected via a Model 310 Adams–Smith Data Interface to a Hewlett–Packard 98136A desk computer. The spectra were digitized at 1 nm wavelength intervals.

SMOOTHING AND DIFFERENTIATION

The numerical values of absorbance and its first and second derivatives used in the calculations were generated from the experimentally measured spectra using numerical smoothing and differentiation methods.

**Smoothing** was done using the Savitzky and Golay method\(^{10,16,17}\) based on least squares
fitting. The smoothed value of the central part of nine equidistant points was calculated using a polynomial of third degree. Four points on each side of the data points are lost in the process.

Smoothing was also done using cubic spline functions\(^{18-22}\) \(S(x)\) which have the following characteristics.

(a) The function \(S(x)\) and its first and second derivatives are continuous.
(b) All the data points \((x_i, y_i), i = 1, 2, \ldots, n,\) are taken as knots, according to Reinsch.\(^{21}\)
(c) \(S(x)\) is represented as follows:

\[
S(x) = P_i(x) = a_i + b_i(x - x_i) + c_i(x - x_i)^2 + d_i(x - x_i)^3
\]  

In other words, the function \(S(x)\) consists of \(n - 1\) segments \(P_i(x)\) called subsplines which are, in our case, all third-order polynomials and approximate the sought interpolate functions within each interval \((x_i, x_{i+1})\).

The continuity conditions require

\[
P_{i-1}(x_i) = P_i(x_i) \quad P_{i-1}^{(1)}(x_i) = P_i^{(1)}(x_i) \quad P_{i-1}^{(2)}(x_i) = P_i^{(2)}(x_i)
\]  

The smoothest possible spline function passing through the data points with maximum accuracy is obtained by minimizing the expression

\[
\int [S^{(2)}(x)]^2 \, dx + g \sum_{i=1}^{n} \left( \frac{S(x_i) - y_i}{\delta y_i} \right)^2
\]  

This leads to the following equation

\[
P_{i-1}^{(3)}(x_i) - P_i^{(3)}(x_i) = 2g \frac{P_i(x_i) - y_i}{\delta y_i}
\]  

\(g\) is a Lagrangian parameter allowing adjustment between closeness of fit and smoothness.

Combining equations (6) and (8), eliminating \(b, c, d\) and assuming that the error for all data points is the same \((\delta y_i = \delta y)\), the following condition is obtained:

\[
y_{i-1} + 4y_i + y_{i+1} = \frac{3}{h^2} (a_{i-2} - 4a_{i-1} + 6a_i - 4a_{i+1} + a_{i+2}) + (a_{i-1} + 4a_i + a_{i+1})
\]  

In equation (9), \(h_1 = x_1 - x_{-1} = h\), i.e. the points are taken to be equidistant. The coefficients \(a_i\) are the points through which the best spline passes, i.e. the points of the smoothed curve, with accuracy \(\pm \delta y\). Rearranging equation (9), we obtain a system of \(n\) equations with \(n\) unknowns:

\[
\gamma a_{i-2} + \beta a_{i-1} + \alpha a_i + \beta a_{i+1} + \gamma a_{i+2} = y_{i-1} + 4y_i + y_{i+1}
\]  

or in matrix notation:

\[
\begin{bmatrix}
\alpha & \beta & \gamma & 0 & 0 & \ldots & 0 & 0 & 0 & 0 & 0 \\
\beta & \alpha & \beta & \gamma & 0 & \ldots & 0 & 0 & 0 & 0 & 0 \\
\gamma & \beta & \alpha & \beta & \gamma & \ldots & 0 & 0 & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 0 & \ldots & \gamma & \beta & \alpha & \beta & \gamma \\
0 & 0 & 0 & 0 & 0 & \ldots & 0 & \gamma & \beta & \alpha & \beta \\
0 & 0 & 0 & 0 & 0 & \ldots & 0 & 0 & \gamma & \beta & \alpha \\
\end{bmatrix}
\begin{bmatrix}
a_1 \\
a_2 \\
a_3 \\
\vdots \\
a_{n-2} \\
a_{n-1} \\
a_n \\
\end{bmatrix}
= 
\begin{bmatrix}
c_1 \\
c_2 \\
c_3 \\
\vdots \\
c_{n-2} \\
c_{n-1} \\
c_n \\
\end{bmatrix}
\]
where
\[
\alpha = 4 + \frac{18 \delta y^2}{gh^3}, \quad \beta = 1 - \frac{12 \delta y^2}{gh^3}, \quad \gamma = \frac{3 \delta y^2}{gh^3}, \quad c_i = y_{i-1} + 4y_i + y_{i+1}, \quad i = 1(1)n \quad (12)
\]
The computer program for solving these equations was based on the Gauss–Seidel method of successive approximations. For the purposes of smoothing, \(x_i\) is identified with the wavelengths \(\lambda_i\), and \(y_i\) with the experimental absorbances \(A_i\).

The two smoothing methods yield comparable results.

**Numerical differentiation** was done using cubic splines. Differentiation of equation (5) yields the expressions
\[
P_i^{(1)}(x) = b_i + 2c_i(x - x_i) + 3d_i(x - x_i)^2
\]
\[
P_i^{(2)}(x) = 2c_i + 6d_i(x - x_i)
\]
\[
P_i^{(3)}(x) = 6d_i
\]

It follows from the continuity conditions that
\[
P_{i-1}(x_i) = a_{i-1} + b_{i-1}(x_i - x_{i-1}) + c_{i-1}(x_i - x_{i-1})^2 + d_{i-1}(x_i - x_{i-1})^3 \quad (14)
\]
\[
P_i(x_i) = a_i + b_i(x_i - x_i) + c_i(x_i - x_i)^2 + d_i(x_i - x_i)^3 \quad (15)
\]

Therefore
\[
a_{i-1} + b_{i-1}h + c_{i-1}h^2 + d_{i-1}h^3 = a_i = P_i(x_i) \quad (16)
\]
where \(h = h_i = (x_i - x_{i-1})\) for all \(i\). Similarly, from the continuity conditions for the derivatives we get
\[
b_{i-1} + 2c_{i-1}h + d_{i-1}h^2 = b_i = P_i^{(1)}(x_i) \quad (17)
\]
\[
c_{i-1} + 3d_{i-1}h = c_i = P_i^{(2)}(x_i) \quad (18)
\]
If the same procedure is repeated for the point \(x_{i+1}\), we obtain five equations, from which the following equation results
\[
b_{i-1} + 4b_i + b_{i+1} = 3(a_{i+1} - a_{i-1})/h \quad (19)
\]

In applying these results for numerical differentiation, \(y_i\) and \(x_i\) are identified with the corresponding \(A_i\) and \(\lambda_i\) of the smoothed curves.

Numerical differentiation of an actual spectrum consisting of \(n + 2\) equidistant points \((\lambda_i, A(\lambda_i)), \quad i = 0, 1, \ldots, (n + 1)\), is performed in the following manner. The smoothed absorbance values are entered for all \(\lambda_i\) in equation (19) to yield a system of \(n\) equations with \(n + 2\) unknowns. Setting \(b_0 = b_{n+1} = 0\), the number of unknowns is reduced to \(n\), which may then be determined to give the first-derivative spectrum.

The second-derivative spectrum is obtained by differentiating the first-derivative spectrum in the same manner.

Differentiation may also be performed by a simple moving point method. This is done by estimating the end point of each segment with a Lagrange interpolation function.23 The first derivative of the central point \((\lambda_i, A(\lambda_i))\) of a nine-point segment is found to be given by
\[
A^{(1)}(\lambda_i) = \frac{1}{2328h} \left[-3A(\lambda_{i-5}) + 26A(\lambda_{i-4}) - 126A(\lambda_{i-3}) + 498A(\lambda_{i-2}) - 1871A(\lambda_{i-1})
\right.
\]
\[
+ 1871A(\lambda_{i+1}) - 498A(\lambda_{i+2}) + 126A(\lambda_{i+3}) - 26A(\lambda_{i+4}) + 3A(\lambda_{i+5})\] \quad (20)
\]
Five points on each side of the data point series are lost in the process.
Both differentiation methods give comparable results. The accuracy of the calculated derivatives for theoretical spectra (no noise) is exceptional.

In summary, from the experimental spectrum, calculations of smoothed absorbance values and first and second derivatives were obtained via the following procedure:

\[ A_{\text{exp}} \xrightarrow{\text{sm}} A_{\text{sm}} \xrightarrow{\text{diff}} A^{(1)}_{\text{sm}} \xrightarrow{\text{sm}} A^{(2)}_{\text{sm}} \]

which yielded low-noise derivatives appropriate for calculating the Wronskian.

RESULTS

The smoothed spectra of the solutions of Cr(acac)₃ (solution 1) and Co(acac)₃ (solution 2) are shown in Figures 1 and 2 respectively. The figures also include the simulation of the

![Figure 1](image1.png)

Figure 1. (1) Absorption spectrum of a $7 \cdot 3 \times 10^{-3}$M Cr(acac)₃ solution in chloroform. (2) Simulation of this spectrum with an asymmetric Gaussian having the parameters quoted in the text. (3) Difference between the experimental and simulated spectra

![Figure 2](image2.png)

Figure 2. (1) Absorption spectrum of a $6 \cdot 5 \times 10^{-3}$M Co(acac)₃ solution in chloroform. (2) Simulation of this spectrum with an asymmetric Gaussian having the parameters quoted in the text. (3) Difference between the experimental and simulated spectra
Figure 3(a). (1) Absorption spectrum of a chloroform solution $5.9 \times 10^{-3}$M in Cr(acac)$_3$ and $1.5 \times 10^{-3}$M in Co(acac)$_3$. (2), (3) The component spectra. (b) (1) Absorption spectrum of a chloroform solution $5.9 \times 10^{-3}$M in Cr(acac)$_3$ and $1.5 \times 10^{-3}$M in Co(acac)$_3$. (2) Simulation with a linear combination of two asymmetric Gaussians. (3) Difference spectrum.

Experimental spectra with asymmetric Gaussians with the following parameters:

<table>
<thead>
<tr>
<th></th>
<th>Cr(acac)$_3$</th>
<th>Co(acac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c \varepsilon_{\text{max}}$ (cm$^{-1}$)</td>
<td>0.4830</td>
<td>0.8207</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>560.5</td>
<td>593.6</td>
</tr>
<tr>
<td>$w(\lambda \geq \lambda_{\text{max}})$ (nm)</td>
<td>108.2</td>
<td>114.0</td>
</tr>
<tr>
<td>$w(\lambda \leq \lambda_{\text{max}})$ (nm)</td>
<td>104.2</td>
<td>106.8</td>
</tr>
</tbody>
</table>

Figure 4(a) Absorption spectrum of a chloroform solution $2.6 \times 10^{-3}$M in Cr(acac)$_3$ and $3.9 \times 10^{-3}$M in Co(acac)$_3$. (2), (3) The component spectra. (b) (1) Absorption spectrum of a chloroform solution $2.6 \times 10^{-3}$M in Cr(acac)$_3$ and $3.9 \times 10^{-3}$M in Co(acac)$_3$. (2) Simulation with a linear combination of two asymmetric Gaussians. (3) Difference spectrum.
From the difference between the experimental and simulated spectra it is clear that the fit in the wavelength range of practical interest is very good. Differences become significant only at the tails.

The spectra of two solutions containing both complexes are given in Figures 3 (solution 3) and 4 (solution 4). These figures also contain the simulation of the spectra using the following linear combinations of the asymmetric Gaussians defined previously:

\[
A_3(\lambda) = 0.811 A_1(\lambda) + 0.223 A_2(\lambda)
\]
\[
A_4(\lambda) = 0.354 A_1(\lambda) + 0.606 A_2(\lambda)
\]

The experimental spectra and their first derivatives were then used to evaluate the \(2 \times 2\) Wronskian determinants of all possible combinations of the four solutions, namely [1, 2] [1, 3] [1, 4] [3, 2] [4, 2] [3, 4]. For the [1, 2] combination, for example, the Wronskian is

*Figure 5. Values of the \(2 \times 2\) Wronskians as a function of the wavelength, estimated using the smoothed experimental data for the six combinations of the four solutions measured. The combination is indicated in brackets on the left of each plot, e.g. \(W[1, 2]\) for the upper left plot, and so on*
given by the expression

\[ W[1, 2] = A_1 A_2^{(1)} - A_2 A_1^{(1)} \]

For the other 2 x 2 Wronskians the expressions are similar.

For estimating all possible 3 x 3 Wronskians, we use the absorbances and their first and second derivatives. Thus for \( W[1, 2, 3] \), for example, the expression is

\[ W[1, 2, 3] = A_1 A_2^{(1)} A_3^{(2)} - A_1 A_3^{(2)} A_2^{(1)} + A_2 A_3^{(1)} A_1^{(2)} - A_2 A_1^{(2)} A_3^{(1)} + A_3 A_1^{(1)} A_2^{(2)} - A_3 A_2^{(2)} A_1^{(1)} \]

The plots of the 2 x 2 Wronskians versus the wavelength are given in Figure 5. It is clear that these determinants do not vanish for all the λs in the interval under investigation. In contrast, in the 3 x 3 Wronskians the pattern collapses (Figure 6); the points are now distributed around zero in a seemingly non-random manner with the following characteristics.

(i) The values tend to be larger in the middle of the wavelength range, i.e. around the peak of the absorbance band, presumably because the error in the difference between large numbers is larger than that between small numbers.

(ii) The plots (Figure 6) contain zigzag segments about the zero value.

These characteristics indicate a systematic error, and in order to find its origin, the following heuristic method was applied.

1. The arithmetic values of the simulated spectra were calculated for the same wavelengths as for the experimental spectra.

2. An error was introduced by rounding off to the third decimal character of the absorbance values of the simulated spectra. This is a simplified way of introducing ‘noise’ comparable to the precision of the experimental spectra, which is ±0.0010 absorbance.
Figure 7(a). Values of the 2 × 2 Wronskians as in Figure 5, but using ‘noisy’ simulated spectra of precision ±0·0010. (b) Values of the 2 × 2 Wronskians as in Figure 5, but using ‘noisy’ simulated spectra of precision ±0·0005 units (a.u.). Thus two series of ‘noisy’ simulated spectra were generated, for assumed precision of ±0·0010 and ±0·0005 a.u.

3. Using both sets of ‘noisy’ simulated spectra, we calculated the absorbances and their first and second derivatives by applying the same procedure used for the experimental spectra.

The 2 × 2 Wronskians from simulated and ‘noisy’ simulated spectra have the same shape as the experimental ones, as can be seen in Figure 7. Figure 8 shows the striking similarity of the 3 × 3 Wronskians calculated from ‘noisy’ simulated spectra and the corresponding experimental ones. In contrast, the 3 × 3 Wronskians calculated from the simulated spectra without ‘noise’ are identically equal to zero.

It has been shown, therefore, that ‘noise’ will cause the 3 × 3 Wronskians to assume small (positive or negative) non-zero values at each wavelength.
Figure 8(a). Values of the $3 \times 3$ Wronskians as in Figure 6, but using 'noisy' simulated spectra of precision $\pm 0.0010$. (b) Values of the $3 \times 3$ Wronskians as in Figure 6, but using 'noisy' simulated spectra of precision $\pm 0.0005$

CONCLUSIONS

The Wronskian determinant has been used to determine the number of components in multicomponent systems from measurements on mixtures. The development of derivative spectroscopy in recent years makes possible the calculation of this determinant from the absorbances and their derivatives.

The advantage of this method compared to linear algebra methods is its generality, and also the fact that it is sensitive to minor components; the number of components can, in principle, be determined by measuring any collective property of the system, provided that the contribution of each component to this property is characteristic and that the problem of the noise has been solved.

In this paper the method is used in conjunction with smoothing and numerical differentiation techniques based on spline functions. Instrumental methods of smoothing would have been more convenient but were not available. The experimental data quoted refer to a two-component system; for this system the spline functions are of the third order. Higher orders are needed for more components.

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APPENDIX

A mixture (composition) \( j \) is characterized by a set of \( n \) numbers \( c_{1j}, c_{2j}, \ldots, c_{nj} \) representing the amounts (percentage or concentration or any extensive property depending uniquely on the amount) of each of the components.

In chemical terminology, from \( n \) different mixtures of the \( n \) components, and not less than \( n \), we can prepare any other mixture. This is the meaning of the linear dependence of the \((n + 1)\)th composition. The number of linearly independent compositions is \( n \), i.e. the same as the number of components. It also follows (see mathematical formulation below) that the number of linearly independent compositions equals the number of linearly independent measurements \( u(x, c_{1j}, c_{2j}, \ldots, c_{nj}) \) of a physical or other collective property.

In mathematical terms, the number representing a given composition can be regarded as the co-ordinates of a point in an \( n \)-dimensional space. Beer–Lambert’s law (equation (2)) then essentially represents a transformation of co-ordinates, in fact an affine transformation,\(^{24} \) i.e. the new variables (the absorbances at each wavelength in this case) are related to the initial ones (the concentrations) linearly. However, in this paper we deal not only with affine transformations but also with non-linear ones, namely transformations to general curvilinear co-ordinates, provided that they are unique, i.e. one-to-one, that to each initial value corresponds one and only one new value.

The requirement that the transformation is one-to-one ensures that the dimension of the space is retained. In practice this means that if we determine the dimension of the space of the absorbances at each wavelength, this will also be the dimension of the space of the concentrations, namely the number of components.

Alternatively, the concentrations \( c_{1j}, c_{2j}, \ldots, c_{nj} \) can be considered as the components of a vector in an \( n \)-dimensional vector space, and it is known\(^{24} \) that such a space is spanned by \( n \) linearly independent vectors; any set of \( n \) linearly independent vectors can be used as bases and any other vector can be expressed as a linear combination of these base vectors.

REFERENCES