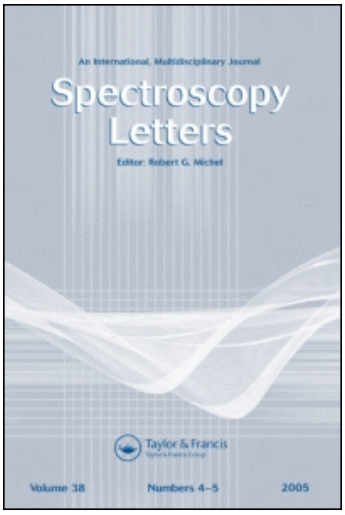

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APPLICATION OF ORTHOGONAL FUNCTIONS IN SPECTROFLUOROMETRIC ANALYSIS

Key Words : Orthogonal functions; Spectrofluorometric analysis; Orciprenaline sulphate determination; guaifenesin determination.

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ABSTRACT

The orthogonal functions method is used to correct for interferences in spectrofluorometric analysis. The method has been applied to the determination of orciprenaline sulphate in the presence of oxazepam and guaifenesin in the presence of sulphadiazine. The results obtained are encouraging and suggest that the method could be used for similar problems.

INTRODUCTION

In The last twenty years, orthogonal functions[1-3] were used extensively in correcting background interferences in spectrophotometric analysis. The method has been used for a wide range of applications in spectro-

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photometry. For examples, in analysis of some weakly absorbing compounds[4], two-component analysis[1, 5], multicomponent analysis[6] and also for the analysis of compounds in the presence of their degradation products[7] and in the presence of other interfering constituents[8,9]. Other modifications for the application of orthogonal functions have been reported. These include the Δp_j method,[10, 11] the combined polynomial method[12] and orthogonal polynomials for unequal intervals[13]. The method has been also extended to correct for interferences in spectropolarimetric analysis[14]. However, up till now the method has not been applied to spectrofluorometry.

In conventional spectrofluorometry[15], a pure fluorescence compound (x) could be determined by selecting certain wavelength of excitation ($\lambda_{ex.}$) at which the intensity of fluorescence emission (F) could be measured at a wavelength of maximum emission ($\lambda_{em.}$). In this respect

$$F_{\lambda_{em.}} = 2.303\ k\ I_0.\ abc_x \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where, I_0 is the intensity of incident radiation, k is the fraction of the incident radiation that is absorbed, this dependent upon instrumental conditions; a is a constant corresponding to absorptivity in spectrophotometry and is dependent upon the substance, b is the pathlength of the solution, c_x is the concentration of x. In practice equation (1) holds up when the concentration is few parts per millions and when abc_x approaches a value of 0.01 or less. The above equation could be rewritten as follows

$$F_{\lambda_{em.}} = K\ c_x \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

where K is an overall constant.

According to Glenn's method of orthogonal functions[1] the fluorescence emission curve, $F(\lambda)$, of a compound (x) can be expanded in terms of orthogonal functions as follows :

$$F(\lambda) = p_0P_0 + p_1P_1 + p_2P_2 + \ldots\ldots + p_nP_n \quad \ldots\ldots (3)$$

where $F(\lambda)$ denotes the fluorescence emission of the sample measured under specified conditions at a wavelength λ that belongs to a set of (n+1) equally-spaced wavelengths, P_j are the orthogonal polynomials[16] and p_j are their respective coefficients which are proportional to the concentration of the compound (x). Thus, by analogy to equation (2)

$$p_j = \alpha_j c_x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where α_j is the coefficient of K.

In the presence of a fluorescence interferences, each observed coefficient is the sum of two terms,

$$p_j = \alpha_j c_x + p_j(z) \quad \ldots\ldots\ldots\ldots\ldots (5)$$

where z denotes the contribution from interferences. By a proper choice of polynomial and range, the number of wavelengths and the mean wavelength, $p_j(z)$ can be arranged to be negligibly small relative to $\alpha_j c_x$. In that case, the concentration c_x is directly proportional to p_j. The procedure for the choice of these assay parameters are similar to those for orthogonal functions in spectrophotometry[1 - 3] and spectropolarimetry[14].

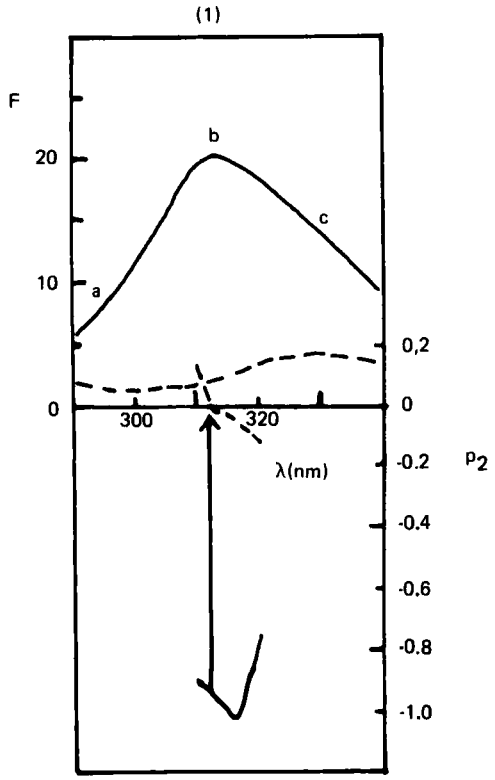
This paper presents an application of the orthogonal function method to the spectrofluorometric analysis. As an illustrative examples, the prescribed pharmaceutical combinations[17] of orciprenaline sulphate with oxazepam and of guaifenesin with sulphadiazine

have been used. The fluorescence characteristics of phenolic and phenoxy compounds[18] in acidic solutions have been adopted in this instance to develop a relatively more sensitive method of analysis for orciprenaline sulphate (phenolic derivative) and guaifenisin (phenoxy derivative) which exhibit strong intrinsic fluorescence relative to oxazepam and sulphadiazine (interferences).

APPLICATION OF THE METHOD

1. For the Determination of Orciprenaline sulphate in the Presence of Oxazepam :

The fluorescence emission curve of orciprenaline sulphate in 0.1 N sulphuric acid was found to possess a maximum fluorescence emission at 314 nm ($\lambda_{ex.}$ 280 nm) (Fig. 1). According to general rules[3,4, 17], the quadratic polynomial, P_2, was chosen as it makes a large contribution to the fluorescence emission curve of orciprenaline sulphate over the segment abc (Fig. 1); hence the coefficient, p_2, should afford precise estimate of concentration. On the other hand, the fluorescence emission curve of oxazepam in 0.1 N sulphuric acid was examined under the same condition. It was found that the quadratic component p_2P_2 made a small contribution to the curve corresponding to the same segment abc (Fig. 1). The correction of such interference of oxazepam in the determination of orciprenaline sulphate can be carried out using the quadratic polynomial, P_2, for 6 points at the specified intervals and range of wavelengths as cited in Table 1. Under these conditions $|p_2|$ is maximal in the convoluted curve of orciprenaline sulphate and negligibly small for the interference (oxazepam).



1- The fluorescence emission curves of 0.2 mg% orciprenaline sulphate (——) and 0.1 mg% oxazepam (----) in 0.1 N sulphuric acid and the p_2 convoluted curves derived therefrom (λ ex 280 nm).

The estimated error as the ratio $p_2(z)/p_2(x)$ was 1.01 % (Table 1).

2. For the Determination of Guaifenesin in the Presence of sulphadiazine.

Figure 2 shows the fluorescence emission curve of guaifenesin and sulphadiazine in 0.1 N sulphuric acid. Guaifenesin was found to possess a maximum fluorescence

Table 1 : Assay parameters for the spectrofluorometric determination of orciprenaline sulphate and guaifenesin using orthogonal function method.

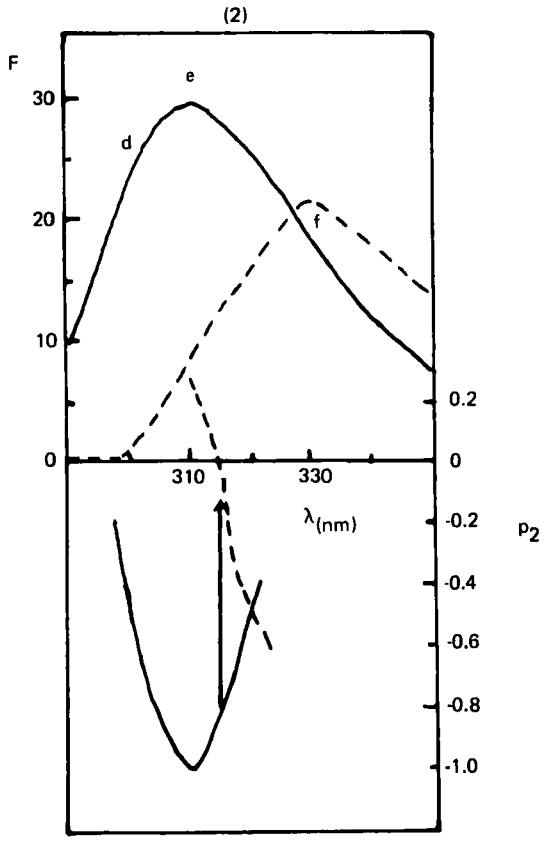
Compound (x)	λ_{ex} (nm)	P_j	No. of points	range (nm)	interval (nm)	mean λ_m (nm)	$\frac{p_j(z)}{p_j(x)}$	% error
Orciprenaline sulphate	280	P_2	6	292-332	8	312	$\frac{-0.0095}{-0.9369}$	1.01
Guaifenesin	275	P_2	6	300-330	6	315	$\frac{-0.0119}{-0.7786}$	1.52

emission at 312 nm ($\lambda_{ex.}$ 275 nm) while that of sulphadiazine was at 330 nm at the same excitation wavelength. The interference due to the contribution of sulphadiazine in the fluorescence emission curve of guaifenesin can be corrected by the application of the quadratic polynomial, P_2, over the segment def (Fig. 2) using 6 points at the intervals and range of wavelengths cited in Table 1. under these conditions the p_2 is maximal in the convoluted curve of guaifenesin and negligibly small for the interference (sulphadiazine) (Fig. 2). The estimated error as the ratio $p_2(z)/p_2(x)$ was 1.52% (Table 1).

EXPERIMENTAL

Apparatus :

The fluorometric measurements were carried out on a Perkin-Elmer Model 650-10S spectrofluorometer equipped with 1 cm quartz cells and a Perkin-Elmer Model 56 recorder. The instrument controls were set as follows: sensitivity range, 0.3 (orciprenaline sulphate) and 0.1 (guaifenesin); slit width, 10 nm for both excitation and emission; response and mode, normal.



2- The fluorescence emission curves of 0.1 mg% guaifenesin (——) and 0.7 mg% sulphadiazine (----) in 0.1 N sulphuric acid and the p_2 convoluted curves derived therefrom (λ_{ex} 275 nm).

Materials :

All drugs used were analytical standards. Other reagents were analytical reagent grade.

General Procedure and Preparation of Calibration Graphs

1. For Orciprenaline Sulphate : A solution of 50 mg of orciprenaline sulphate in 100 ml 0.1 N sulphuric acid

was prepared. Ten ml portion of this solution was diluted to 100 ml with 0.1 N sulphuric acid. 2-6 ml portions of the final diluted solution were diluted to 100 ml with 0.1 N sulphuric acid. The fluorescence emission of each solution was measured at the wavelength range cited in Table 1 using λ_{ex} 280 nm. The coefficient, p_2, was calculated using the following expression :

$$p_2 = [F_0(+5) + F_1(-1) + F_2(-4) + F_3(-4) + F_4(-1) + F_5(+5)] /84$$

where the subscripts 0, 1, 2,.....,5 represent 292, 300,.....332 nm.

2. For Guaifenesin: A solution of 40 mg of guaifenesin in 100 ml distilled water was prepared. Ten ml portion of this solution was diluted to 100 ml with 0.1 N sulphuric acid. 1.5-3.5 ml portions of the final diluted solution were diluted to 100 ml with 0.1 N sulphuric acid. The fluorescence emission of each solution was measured at the wavelength range cited in Table 1 using λ_{ex} 275 nm. The coefficient, p_2, was calculated using the following expression :

$$p_2 = [F_0(+5) + F_1(-1) + F_2(-4) + F_3(-4) + F_3(-1) + F_5(+5)] /84$$

where subscripts 0, 1, 2, ...5 represent 300, 306, 312, ...330 nm.

RESULTS AND DISCUSSION

Under the described experimental conditions, a linear correlation was obtained between p_j and concentration, c, of orciprenaline sulphate and/or

Table 2 : Spectrofluorometric determination of orciprenaline sulphate in the presence of oxazepam and guaifenesin in the presence of sulphadiazine.

Sample	Added orciprenaline sulfate[a] (mg%)	% Recovery		Added guaifenesin.[b] (mg%)	% Recovery	
		Proposed	$F_{max.}$[c]		Proposed	$F_{max.}$[d]
1	0.10	100.7	133.1	0.06	97.8	126.7
2	0.15	99.7	121.1	0.08	98.8	119.0
3	0.20	100.3	117.2	0.10	99.0	116.6
4	0.25	99.3	112.3	0.12	99.8	114.3
5	0.30	101.1	111.2	0.14	99.3	111.9
Mean $\pm$ s.d.		100.3$\pm$0.8			98.9$\pm$0.7	

[a] Each sample contains 0.1 mg% oxazepam.

[b] Each sample contains 0.7 mg% sulphadiazine.

[c] λ_{em} 314 nm (λ_{ex} 280 nm).

[d] λ_{em} 312 nm (λ_{ex} 275 nm).

guaifenesin over the range 0.1-0.3 mg% w/v and 0.06-0.14 mg% w/v, respectively. The linear equations were found to be :

$|p_2| = -0.0076 + 4.714\ c$ ($r = 0.9999$) for orciprenaline sulphate and

$|p_2| = 0.006 + 7.7260\ c$ ($r = 0.9999$) for guaifenesin.

The relative standard deviation for the determination of these drugs in 5 separate determinations was less than 1% indicating reasonable reproducibility.

In order to prove the validity and applicability of the proposed method, 5 synthetic mixtures of orciprenaline sulphate and oxazepam and of guaifenesin and sulphadiazine were prepared and assayed using the proposed method. The results obtained (Table 2) are both precise and accurate.

For comparison, recoveries were calculated from the maximum fluorescence emission ($F_{max.}$) and were unacceptably high (Table 2). The error in each result decreased with increase in the concentration of orciprenaline sulphate or guaifenesin relative to the concentration of interfering compound.

As will have been gathered from the above discussion the correction of interferences in spectrofluorometric analysis can be successfully carried out using Glenn's method of orthogonal functions.

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