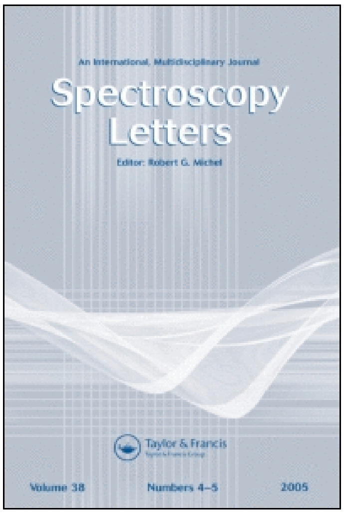

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# Spectral K-Ratio Spectrophotometry

Liu Guomin[a]; Song Gengxin[a]; Zhou Xiaodong[a]
[a] Department of Applied Chemistry, Fushun Petroleum Institute, Fushun, Liaoning Province, China

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# SPECTRAL K-RATIO SPECTROPHOTOMETRY

Key Words: Spectral K-ratio; interference; two components;

spectrophotometry.

Liu Guomin*, Song Gengxin and Zhou Xiaodong

Department of Applied Chemistry
Fushun Petroleum Institute
Fushun, Liaoning Province, 113001, China

## ABSTRACT

A method called "Spectral K-ratio spectrophotometry" was proposed. The method takes the K-coefficient dual-wavelength spectrophotometric method as the mathematical model in order to resolve the different nth-derivative spectral data at one wavelength to determine certain two components systems that their zeroth- (absorption) and nth-derivative spectra were all interfered seriously. Examples of the application of the proposed method were given.

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*Author to whom correspondence should be addressed.

## INTRODUCTION

The requirements of a satisfactory analytical method are usually manifold, but certainly selectivity must be counted among the most important. Hence there has always been interest in procedures that can improve the selectivity of the measurement methods themselves. Among the most conceptually simple of these methods is derivative spectroscopy. It is becoming increasingly porpular as a resolution enhancement technique, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences,[1~3] but the advantage of derivative measurements depents strongly on the relative widths of the interferent and analyte bands. Derivative spectroscopy has been profitably applied to quantitative analytical applications in which the presence of a broad, unstructured background spectrum overlaps the bands of the analyte.[3] F.A. El-Yazbi et al. had used derivative spectrophotometric method to determine three tranquilizer-antidepressant mixtures.[4] Hesham Salem et al. also used U.V.and U.V.first and second derivative spectrophotometric methods with applying "Zero-Crossing" technique of measurement to determine two-component mixtures.[5] Basilio Morelli also recommended the "zero -crossing" derivative spectrophotometry for two-component mixtures.[6,7] But when the absorption spectra and the derivative spectra are all interfered seriously, the determination of the analyte will be very difficult.

Yahya et al. adopted multiwavelength first- and second-derivative spectra with matrix least-squares data processing to resolve mixtures of components with overlapping absorption spectra.[8] This illustrated that the appropriate mathematical resolving of derivative spectra is one of the effective methods. Solving two or three simultaneous equations had been used to determine two or three component mixtures.[9,10] Li et al. also proposed a method called "Combined derivative spectrophotometry" for the simultaneous determination of multicomponent.[11]

This paper proposed a conceptually simple method named "Spectral K--ratio spectrophotometry". It takes the K-coefficient dual wavelengths spectrophotometric method as the mathematical modle in order to resolve the different nth-derivative spectral data at one wavelength to determine some two-component systems that their zeroth-derivative (absorption) and nth-derivative spectra were all interfered seriously. The method was proved by using two sets laboratory prepared mixtures.

## THEORETICAL

Let us consider a complex system containing two components M and N. Their zero-th derivative and n-th derivative spectra overlap seriously, as Fig. 1 shown.

If at $\lambda_1$, the derivative values ( zero-th and n-th ) of M and N comply with Beer's law and possess additive property, the following will be true:

$$D^0 = D^0_M + D^0_N \qquad (1)$$

$$D^n = D^n_M + D^n_N \qquad (2)$$

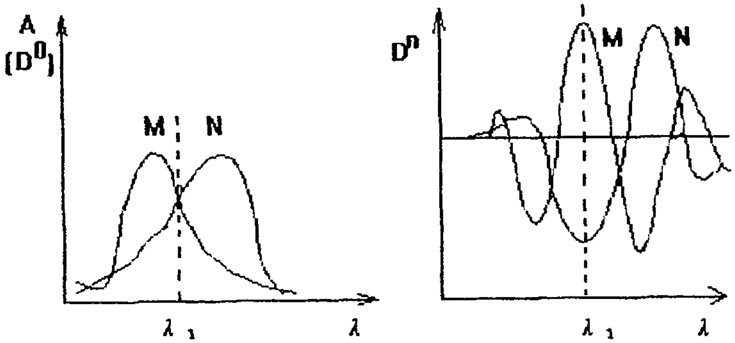

Fig.1. The zeroth- (absorption) and nth-derivative spectra of M and N.

Here, $D^0$ and $D^n$ are the derivative values of the system at $\lambda_1$; $D^0_M$ and $D^n_M$ are the zero-th and n-th derivative value of M at $\lambda_1$ respectively; $D^0_N$ and $D^n_N$ are those of N at $\lambda_1$ respectively.

Let $K_N = \frac{D^n_N}{D^0_N}$, and equation (1) mutiplied by $K_N$, equation (3) was obtained:

$$K_N * D^0 = K_N * D^0_M + K_N * D^0_N \qquad (3)$$

subtract equation (3) from equation (2), we obtained equation (4):

$$\Delta D = D^n - K_N * D^0 = D^n_M - K_N * D^0_M \qquad (4)$$

We all know that $K_N$ is a constant, so,the value of $\Delta D$ is only related to the derivative values of M. Hence we could determine M by using $\Delta D$ eliminating the interference of N. By selecting a such wavelength that $D^n_M$ possesses the sign digit opposit to that $K_N$ possesses,the absolute value of $\Delta D$ would be larger. Hence, not only the two-component mixture can be determined,but also the sensitivity of the determination can be enhanced. Similarly, the equation to determine N can be deduced:

$$\Delta D = D^{n} - K_{M} * D^{o} = D^{n}_{N} - K_{M} * D^{o}_{N} \qquad (5)$$

The determination of $K_N$ or $K_M$ is important. In specific determination, we adopt the method proposed by Ni et al.[12] It is a method to determine simutaneously the coefficient K and the slope of the calibration curve by linear plot means for dual-wavelength absorption determination. The deviation of absorption resulting from molecular interaction can be calibrated by this method and the accuracy is increased. We modified this method to suit with our purpose. The following is the theoretical. According to equation (4), we have (6):

$$D^{n} - K_{N} * D^{o} = ( d_{M} - K_{N} * k_{M} ) C_{M} \, l \qquad (6)$$

here, according to Beer's law, $d_M$ and $k_M$ are constant, $C_M$ is the concentration of M, l is the light path of the sample.

Equation (6) divided by $D^o$, we have:

$$\frac{D^{n}}{D^{o}} - K_{N} = ( d_{M} - K_{N} * k_{M} ) * \frac{C_{M} * l}{D^{o}} \qquad (7)$$

Let $Y = D^{n}/D^{o}$ , $k = d_{M} - K_{N} * k_{M}$ , $x = ( l * C_{M} ) / D^{o}$ ,

we obtained:

$$Y = k\,x + K_{N} \qquad (8)$$

here, $K_N$ is the ratio $D^{n}_{N}/D^{o}_{N}$, k is the slope of the calibration curve to determine M. It is obvious that by regression of $D^{n}/D^{o}$ to $C_{M} * l/D^{o}$, we can obtaine the two critical parameters for determination of M. Similarly, we have:

$$Y = kx + K_M \qquad (9)$$

here, $K_M$ is the ratio $D^n_M/D^o_M$, k is the slope of the calibration curve to determine N.

## EXPERIMENTAL

In this section, we demonstrate the application of the proposed method on two sets of data.

### Apparatus

The Perkin-Elmer Model Lambda 9 UV/VIS/NIR Spectrophotometer was used. The spectra were recorded in 1 cm quartz cuvettes. The instrument settings are: scan speed 960nm/min; spectral slit width 2nm; chart speed 60 mm/min; $\Delta\lambda$ □ 3nm.

### Reagents

All the chemicals used were of analytically pure grade and water was distilled water.

The spectra of thymol, salicylic acid and 4-nitrobenzoic acid were shown in Fig.2.

### Solutions

Aqueous solutions (containing 2% methyl alcohol in volume percent) of thymol, salicylic acid and 4-nitrobenzoic acid were prepared by weighing correspondent reagent as stock solutions.

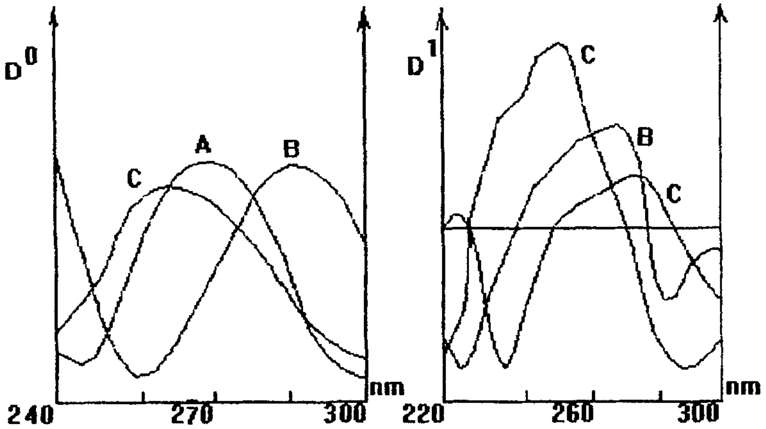

Fig. 2. The absorption and first-derivative spectra of thymol (A), salicylic acid (B) and 4-nitrobenzoic acid (C).

## Procedure

Prepare the aqueous solutions (containing 2% methyl alcohol in volume percent) of thymol and salicylic acid at different concentration level and those of thymol and 4-nitrobenzoic acid at different concentration with the correspondent stock solutions.

Then record the spectra against the reagent blank at 282 nm. Calculate the ratio $K_N$ and $K_M$, the slope of the calibration curve for M and N respectively, by regressing the spectral data.

With the obtained calibration curve, determine a serious samples that their concentrations were already known.

TABLE 1

Results of the determination of thymol (A) and salicylic acid (B).

| No. | Concentration prepared $*10^{-4}$M/L |  | Concentration determined $*10^{-4}$M/L |  | Average concentration determined $*10^{-4}$M/L |  | Standard deviation $*10^{-6}$ |  | Variation coefficient (%) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  | A | B | A | B | A | B | A | B | A | B |
| 1 | 0.6169 | 7.473 | 0.5922; 0.5799; 0.5799 | 7.446; 7.465; 7.449 | 0.5840 | 7.453 | 0.7101 | 1.022 | 1.216 | 0.1371 |
| 2 | 1.234 | 6.686 | 1.201; 1.197; 1.209 | 6.714; 6.706; 6.722 | 1.201 | 6.714 | 0.6112 | 0.8000 | 0.5089 | 0.1192 |
| 3 | 2.056 | 5.900 | 2.040; 2.044; 2.048 | 5.967; 5.975; 5.978 | 2.044 | 5.975 | 0.4000 | 0.5701 | 0.1957 | 0.09541 |
| 4 | 2.879 | 5.113 | 2.891; 2.916; 2.895 | 5.204; 5.219; 5.208 | 2.899 | 5.211 | 1.343 | 0.7772 | 0.4633 | 0.1491 |
| 5 | 3.701 | 4.327 | 3.734; 3.726; 3.730 | 4.460; 4.441; 4.448 | 3.730 | 4.448 | 0.4000 | 0.9612 | 0.1072 | 0.2161 |
| 6 | 4.524 | 3.540 | 4.594; 4.459; 4.594 | 3.638; 3.634; 3.638 | 4.549 | 3.638 | 0.0000 | 0.2324 | 0.0000 | 0.06388 |
| 7 | 5.346 | 2.753 | 5.396; 5.412; 5.412 | 2.848; 2.840; 2.840 | 5.408 | 2.844 | 0.9241 | 0.4621 | 0.1709 | 0.1625 |
| 8 | 6.169 | 1.967 | 6.214; 6.227; 6.259 | 2.030; 2.030; 2.002 | 6.235 | 2.022 | 2.316 | 1.617 | 0.3715 | 0.7997 |
| 9 | 6.992 | 1.180 | 7.053; 7.033; 7.037 | 1.188; 1.156; 1.160 | 7.041 | 1.168 | 1.058 | 1.744 | 0.1503 | 1.493 |
| 10 | 7.814 | 0.5900 | 7.851; 7.843; 7.851 | 0.5270; 0.5152;0.5270 | 7.847 | 0.5231 | 0.4637 | 0.6813 | 0.8864 | 1.302 |

TABLE 2

Results of the determination of thymol (A) and 4-nitrobenzoic acid (C).

| No. | Concentration prepared $*10^{-4}$M/L | | Concentration determined $*10^{-4}$M/L | | Average concentration determined $*10^{-4}$M/L | | Standard deviation $*10^{-6}$ | | Variation coefficient (%) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A | C | A | C | A | C | A | C | A | C |
| 1 | 0.6078 | 1.510 | 0.6281; 0.7092; 0.6443 | 1.568; 1.481; 1.501 | 0.6605 | 1.497 | 4.292 | 4.557 | 6.498 | 3.044 |
| 2 | 1.216 | 1.351 | 1.208; 1.163; 1.220 | 1.357; 1.376; 1.357 | 1.195 | 1.363 | 3.005 | 1.097 | 2.515 | 0.8048 |
| 3 | 2.026 | 1.192 | 1.986; 1.982; 1.990 | 1.205; 1.202; 1.208 | 1.986 | 1.205 | 0.4000 | 0.3000 | 0.2014 | 0.2490 |
| 4 | 2.837 | 1.033 | 2.816; 2.788; 2.792 | 1.047; 1.054; 1.047 | 2.800 | 1.049 | 1.514 | 0.4044 | 0.5407 | 0.3855 |
| 5 | 3.647 | 0.8742 | 3.530; 3.594; 3.594 | 0.9132; 0.8917;0.8917 | 3.574 | 0.8989 | 3.695 | 1.241 | 1.034 | 1.381 |
| 6 | 4.458 | 0.7153 | 4.433; 4.431; 4.441 | 0.7280; 0.7264;0.7240 | 4.431 | 0.7264 | 0.5292 | 2.014 | 0.1134 | 2.774 |
| 7 | 5.268 | 0.5563 | 5.248; 5.223; 5.248 | 0.5675; 0.5691;0.5619 | 5.240 | 0.5659 | 1.443 | 3.781 | 0.2754 | 6.681 |
| 8 | 6.078 | 0.3974 | 6.111; 6.074; 6.074 | 0.3990; 0.3998;0.3998 | 6.086 | 0.3998 | 2.137 | 0.4626 | 0.3511 | 1.157 |
| 9 | 6.889 | 0.2384 | 6.917; 6.913; 6.917 | 0.2231; 0.2337;0.2297 | 6.917 | 0.2321 | 0.2345 | 0.5353 | 0.03390 | 2.306 |
| 10 | 7.699 | 0.1192 | 7.744; 7.744; 7.728 | 0.1105; 0.1105;0.1113 | 7.740 | 0.1105 | 0.9247 | 0.4618 | 0.1195 | 4.179 |

## RESULTS AND DISCUSSION

### The determination of the calibration curve

I. For the mixture of thymol and salicylic acid

(i.) The analyte is thymol

$Y = -2.528\,x + 13.30 \qquad \gamma = -0.9999$

$K_N = 13.30 \qquad \Delta D = -2.528\,C_M$

(ii.) The analyte is salicylic acid

$Y = 3.305\,x - 29.81 \qquad \gamma = 0.9994$

$K_M = -29.81 \qquad \Delta D = 3.305\,C_N$

II. For the mixture of thymol and 4-nitrobenzoic acid

(i.) The analyte is thymol

$Y = -1.422\,x - 4.912 \qquad \gamma = 0.9999$

$K_N = -4.912 \qquad \Delta D = -1.422\,C_M$

(ii.) The analyte is 4-nitrobenzoic acid

$Y = 1.765\,x - 29.89 \qquad \gamma = 0.9996$

$K_M = -29.89 \qquad \Delta D = 1.765\,C_N$

### The determination of the samples prepared

Using the method proposed, the samples prepared with the known concentration were determined. The results were listed in Table 1 and Table 2. The results agree well with those of the prepared.

## CONCLUSIONS

This paper showed a variant application of the K-coefficient idea. The method is simple and applicable to some two-component mixtures that the derivative spectra (zeroth- and nth-) of the two components in the mixture were all interfered seriously. The method was not intended as a replacement for other methods but rather as an alternative tool. So far, it was developed for two components, but it can be extended to three or more components with certain restricted conditions.

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