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RESEARCH ARTICLE

Measurement analysis of two radials with a common-origin point and its application

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Abstract

In spectral analysis, a chemical component is usually identified by its characteristic spectra, especially the peaks. If two components have overlapping spectral peaks, they are generally considered to be indiscriminate in current analytical chemistry textbooks and related literature. However, if the intensities of the overlapping major spectral peaks are additive, and have different rates of change with respect to variations in the concentration of the individual components, a simple method, named the 'common-origin ray', for the simultaneous determination of two components can be established. Several case studies highlighting its applications are presented.

KEYWORDS

common-origin ray, measurement analysis, overlapped spectral peaks, simultaneous determination, two components

1 | INTRODUCTION

Spectral analysis is a powerful tool with which to identify and measure chemicals from their characteristic spectra, usually from the characteristic peak of the spectra. In most cases, only one major peak is selected. In this respect, several cases are discussed in standard analytical chemistry textbooks, as detailed below.

For a single-component system, spectral quantitative analysis is conducted using the standard curve method. At wavelength λ of the selected major intensity peak, a series of concentrations x of standard substances is prepared and the corresponding spectral intensities y are scanned. The functional relation (x, y) is expressed by a straight line as the standard curve. When unknown samples are measured, their spectral intensities are located within the range of the standard curve. Thus, a certain spectral signal intensity, y, can be directly related to the corresponding content of the sample (or abscissa value x). The normalized correlation coefficient, r, is the degree of matching between the experimental measurement and the standard curve.[1–7]

Three cases of spectral quantitative analysis are shown in Figure 1(a–c) for a two-component system.

In Figure 1(a), the characteristic peaks at wavelengths λ_1 and λ_2 for the two components are completely non-overlapping. Their concentrations can be determined using the standard curve methods in sequence, just as in the single-component system.

In Figure 1(b), the spectral peaks overlap partially. The content of samples can be determined using dualistic linear equations based on the actual measurements at characteristic peaks 1 (λ_1) and 2 (λ_2). The prerequisite is that the spectral intensities of the two components are additive.[6,8,9]

In Figure 1(c), the spectral peaks of the two components overlap completely at the same characteristic wavelength ($\lambda_1 = \lambda_2$). In this case, and as stated in current textbooks,[8–10] the two components cannot be determined simultaneously.

Abbreviations used: AM, Ammonium; β-CD, β-Cyclodextrin; CPZ, chlorpromazine; a-N, a-Naphthol; β-N, β-Naphthol; PA, Phenylalanine; PBS, Phosphate-buffered saline; PZ, Promethazine hydrochloride; QD, Quantum dot; RRS, Resonance Rayleigh scattering; Try, Tryptophan; UV, Ultraviolet; Vis, Visible.

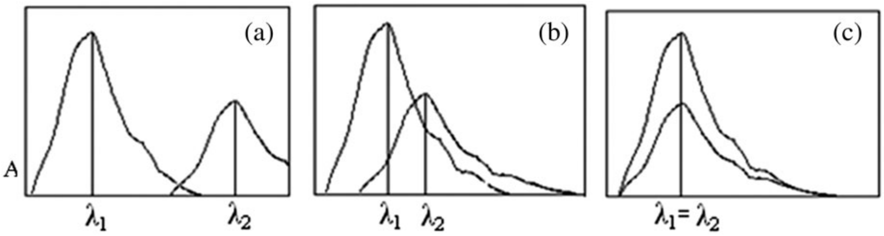

FIGURE 1 Three cases of spectral quantitative analysis of a two-component system

In this study, a simple and operative method to identify and measure individual concentrations of two components with completely overlapping spectral peaks was developed, provided that the characteristic peaks of the two components at the same wavelength (λ): (a) are additive; (b) have different rates of change with respect to variations in their concentrations; and (c) the total of the two concentrations is known or can be obtained indirectly. This spectral analysis method is easy to operate and calculate with reliable results, and can be used for various spectral measurements such as fluorescence spectra, ultraviolet–visible (UV–vis) absorption spectra or resonance Rayleigh scattering (RRS) spectra. A patent has been applied for. The method provides a solution to the problem of completely overlapping spectra of two components in molecular spectroscopy. It is especially suitable for the simultaneous determination of two-component isomers with similar physical and chemical properties, or optical isomers in environmental monitoring, pharmaceutical analysis and quality control.

In the past, this ‘common-origin ray’ has been used for the simultaneous determination of two components, and this is discussed in detail below. However, a description of the ‘common-origin ray’ has not been published to date, and this paper is the first paper to explain the ‘common-origin ray’.

2 | COMMON-ORIGIN RAY OF TWO RADIALS

2.1 | Mathematical description of the analytical model

The mathematical description of the common-origin ray for two radials is as follows. As shown in Figure 2, the spectral intensities of two isomers x_1 and x_2 can be obtained in terms of the linear standard curves of the two pure substances. According to the Lambert–Beer law, the standard curve of the mixture is also linear, and the measured values of the mixture inevitably fall within the range of the fan-shaped area. The mixing ratio can be calculated in accordance with the ‘common-origin ray’. The calculation is discussed in the following two cases.

a. The two radials have different slopes and interceptions.

$$\begin{cases} Y_1 = a_1x_1 + b_1 \\ Y_2 = a_2x_2 + b_2 \end{cases}$$

when the mixture is x_1 only, then $x_1 = (Y_1 - b_1)/a_1$, with its spectral value on the radial Y_1.

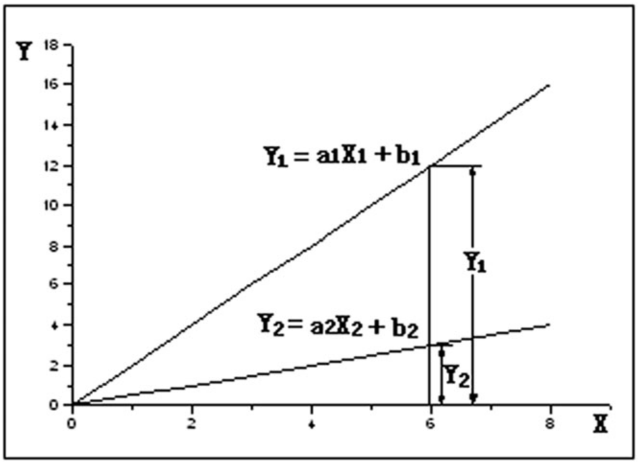

FIGURE 2 Analysis of two radials with a common-origin point

When the mixture is x_2 only, then $x_2 = (Y_2 - b_2)/a_2$, with its spectral value on the radial Y_2.

When the mixture is x (known) and $x = x_1 + x_2$, then:

$$\begin{cases} x_1 = \dfrac{(a_1x_1 + b_1 + a_2x_2 + b_2) - Y_2}{Y_1 - Y_2} \ldots\ldots\ldots\ldots(1) \\ x_2 = x - x_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2) \end{cases}$$

The two concentrations can be calculated from equations (1) and (2). The experimentally measured value would fall into the fan-shaped area formed by the two common-origin ray, and the recovery can be also obtained from the ratio of the experimental value and the calculated value.

The two curves are straight lines with no crossing of the coordinate origin. But the model is also called a ‘common-origin ray’.

b. The two radials cross the origin with different slopes, but the intercepts are same, that is to say b_1 and b_2 in equation (1) are zero.

When the mixture consists of x_1 and x_2, and the total amount $x = x_1 + x_2$, then.

$$\begin{cases} x_1 = \dfrac{(a_1x_1 + a_2x_2) - Y_2}{Y_1 - Y_2} \ldots\ldots\ldots\ldots(3) \\ x_2 = x - x_1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4) \end{cases}$$

As in case a, according to the ‘common-origin ray’, simultaneous determination could be achieved.

2.2 | The concept and connotation of the ‘common-origin ray’

On scanning the known spectra of two pure components and plotting their standard curves, the two radials intersect at the same point for the lowest concentration, whereas they radiate outwards towards the high concentration to form a fan-shaped area, which is the concept of the common-origin ray. The quantitative analysis connotation is that, although the spectral peaks of the two components are spectrally additively overlapped, the signal intensities increase at different rates with respect to their increasing concentrations, and the measured spectral intensities of the two-component mixture inevitably fall within the fan-shaped area. The value of the abscissa is the total concentration of the mixture, and the content of the two components can be calculated based on a graphical method of the linear equations. This method is simple and accessible, and can be used with similar analyses problems that have not been solved to date in the literature.[11–17]

3 | EXAMPLES OF APPLICATIONS

Example 1. Simultaneous determination of D-tryptophan and L-tryptophan by various spectral analysis using the proposed method.

Inclusion complexes of chiral recognition can be formed using β-cyclodextrin (β-CD) with D-tryptophan (D-Try) and L-tryptophan (L-Try), and the analytical method described here is used to determine them simultaneously.[18] The method includes the steps given below.

Step a.

When non-enantiomer inclusion compounds of β-CD with D-Try and L-Try are formed, the characteristic RSS spectral peaks are both located at 278 nm. The increased scattering light intensity of the L-Try + β-CD inclusion compound is strong, whereas that of the D-Try + β-CD inclusion compound is weak.

Step b.

A series of standard solutions of diastereomeric inclusion complex were prepared using the standard substances β-CD, D-Try and L-Try. The spectral intensities of the two standard solutions were measured. Two *I* ~ *C* standard curves were plotted, and the two standard curves (I and II) were entered into the same *I* ~ *C* coordinate system, namely, the spectral analysis model (see Figure 3) for the simultaneous determination of D-Try and L-Try.

Step c.

Determination of the D-Try and L-Try content in the mixture falls within the fan-shaped area formed by the two standard curves (see Figure 4).[19] The abscissa of the value corresponds to the total concentration, *C* (where *C* could be calculated using the interpolation method based on a series of D-Try and L-Try mixture samples) of the D-Try and L-Try mixture, and the content ratio of D-Try and L-Try, C_I: C_{II} equals $(I - I_{II})$:$(I_I - I)$, thus the content of D-Try and L-Try can be calculated. So the simultaneous determination of two-component mixtures can be obtained without the need for separation.

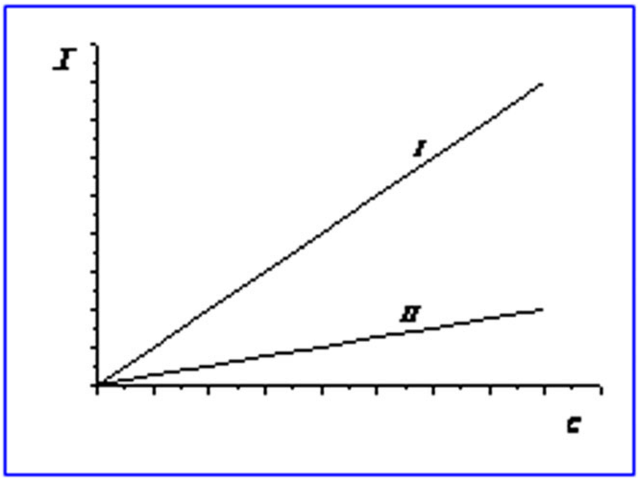

FIGURE 3 Spectral analysis model of two radials with a common-origin point for standard curves with two-component overlapping

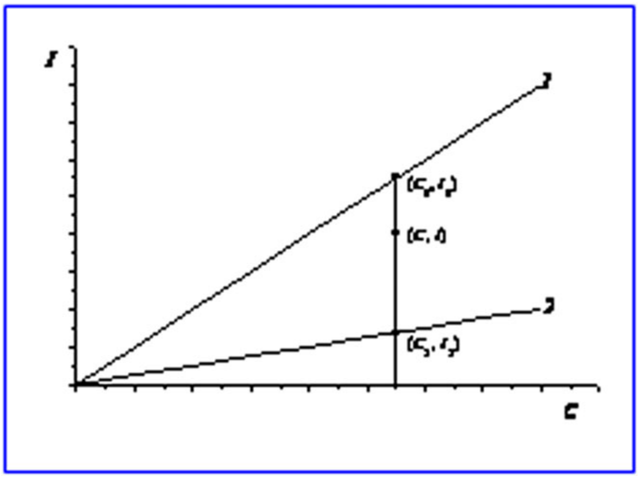

FIGURE 4 The measure proportion model of the two-component system Figure has been reprinted with permission from [Journal of Analytical Science. 8, 454-457 (2006)]. Copyright [2006], In Chinese

Similarly, the nonlinear second-order scattering spectral peaks of D-Try and L-Try inclusion compounds are both located at 556 nm, but the peak amplitude ratio of the L-Try compound is greater than that of the D-Try compound. So, 556 nm can be selected as the measurement wavelength; the spectral analysis model can then be established for the simultaneous determination of D-Try and L-Try using nonlinear second-order scattering spectroscopy. The remaining steps are same as steps a, b and c above.

In addition, the UV–vis absorption spectral peaks of D-Try and L-Try inclusion compounds are both located at 278 nm, the UV–vis absorption intensity of D-Try increased slightly with the increase in its concentration, whereas the intensity of L-Try decreased gradually with the increase in its concentration. So, 278 nm can be selected for the measurement wavelength, and the spectral analysis model can be established for the simultaneous determination of D-Try and L-Try using UV–vis absorption spectroscopy. The other steps are the same as the above-mentioned steps a, b and c.

Example 2. Simultaneous determination of α-naphthol and β-naphthol by RRS with the methods

Isomer inclusion complexes of α-naphthol (α-N) and β-naphthol (β-N) with β-CD can be formed, and using this analytical method, α-N and β-N can be determined simultaneously.

Under optimal conditions (borate–HCl buffer solution, pH 8.2, and a β-CD concentration of 1.8×10^{-3} mol·L^{-1}), conformation of α-N and β-N inclusion complexes, β-N shows a prominent resonance fluorescence spectrum peak at 338 nm, and its intensity increases rapidly with its concentration. By contrast, α-N has a resonance scattering peak at 338 nm, and its intensity increases slowly with its concentration. Thus, a spectral analysis model can be established for the simultaneous determination of α-N and β-N at 338 nm using RRS analysis and the described method (see Figure 5).[20] The remaining steps are the same as steps a, b and c in Example 1.

The resonance fluorescence peaks of α-N and β-N are both at 338 nm; in fact, the two peaks overlap completely, but the spectral intensity shows different rates of change with variations in their concentrations. The peak can, therefore, be drawn out into two standard curves as two common-origin rays for the described invention analytical method. A gross of mixture of α-N and β-N can be determined at 470 nm because changes in the RRS spectral intensity are coincident at 370 to 650 nm.

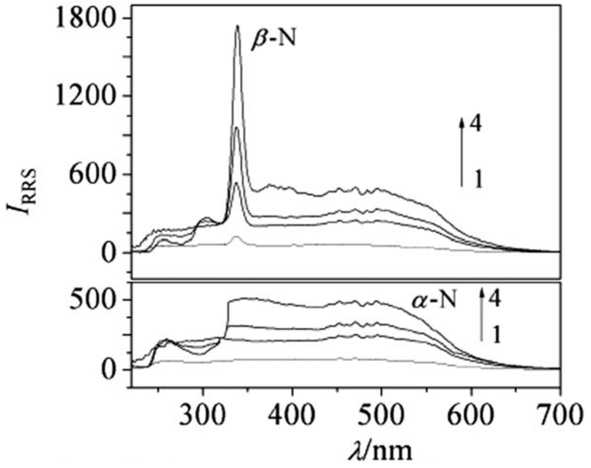

FIGURE 5 RRS spectra of β-CD inclusion compounds of naphthols (from curve 1 to 4, the concentrations of the naphthols are 0.05, 0.05, 1.30 and 3.10×10^{-4} mol·L^{-1}; the concentration of β-CD is 1.8×10^{-3} mol·L^{-1}) Figure has been reprinted with permission from [Chemistry. 7, 539-544 (2008)]. Copyright [2008], In Chinese

Example 3. Simultaneous determination of two homologs as chlorpromazine and promethazine hydrochloride by RRS with the method

Both chlorpromazine (CPZ) and promethazine hydrochloride (PZ) can react with ammonium to form similar ion-association complexes, and CPZ and PZ can be determined simultaneously by using this analytical method.[21]

Under optimal conditions (1 mL of HCl–NaAc buffer solution, pH 1.1; and an ammonium concentration of 1.0×10^{-4} mol·L^{-1}), both CPZ and PZ react with ammonium to form ion-association complexes with RRS peaks at 365 nm; the spectral distinction is due to the different amplification between the two RRS spectrum peak intensities with increasing concentrations of CPZ and PZ. So, it is possible to establish a spectral analysis model for the simultaneous determination of CPZ and PZ at 365 nm (see Figure 6).[22] The remaining steps are the same as step a, b and c in Example 1.

Example 4. Simultaneous determination of Eu(III) and Ce(IV) by fluorescence quenching and measurement analysis of two radials with a common-origin point

In Britton–Robinson buffer solution (pH 3.35–3.85), Eu(III) and Ce(IV) react with famciclovir to form complexes that result in the fluorescence quenching of famciclovir. The maximum excitation wavelength is at 304 nm, and the maximum emission wavelength is at 370 nm. The decreased fluorescence intensities are proportional to the concentrations of Eu(III) and Ce(IV) over certain ranges. However, their linear amplification differed greatly with their concentrations. Based on the differences and additivity of the fluorescence intensities of Eu(III) and Ce(IV), an original radial measurement analysis method for the simultaneous determination of Eu(III) and Ce(IV) was developed using fluorescence spectroscopy (see Figure. 7).[23] The other steps are the same as steps a, b and c in Example 1.

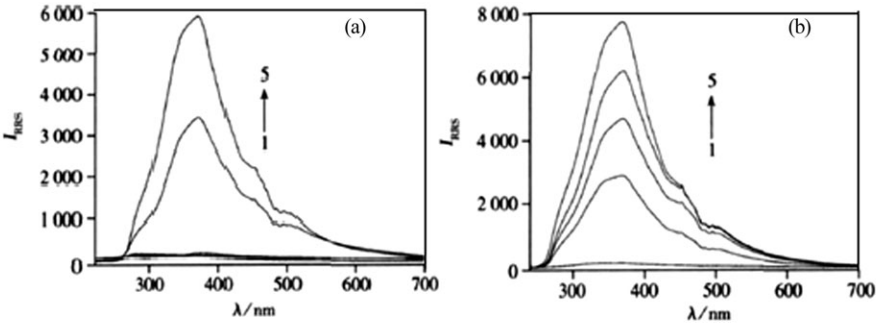

FIGURE 6 RRS spectra of CPZ, PZ and ammonium (AM) system. (a) 1, AM; 2, PZ; 3, CPZ; 4, AM–PZ; 5, AM–CPZ; $C_{AM} = 1.0 \times 10^{-4}$ mol·L^{-1}, $C_{PZ} = C_{CPZ} = 1.0$ mg·L^{-1}. (b) 1–5: $C_{(CPZ+PZ)} = 0, 0.6, 0.8, 1.0$ and 1.2 mg·L^{-1}; $C_{AM} = 1.0 \times 10^{-4}$ mol·L^{-1}) Figure has been reprinted with permission from [Journal of Instrumental Analysis. 12, 1362-1367 (2008)]. Copyright [2008], In Chinese

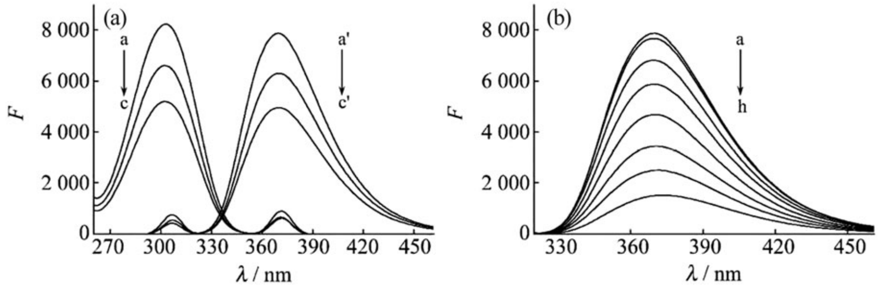

FIGURE 7 Fluorescence spectra of the reaction system (a) A, A′: FCV; B, B′: FCV + Ce (IV); C, C′: FCV + Eu(III); $C_{FCV} = 5.6 \times 10^{-6}$ mol·L^{-1}; $CCe_{(IV)} = C_{Eu(III)} = 1.0$ μg·mL^{-1}; pH = 3.6. (b) A–H: $C_{(Ce(IV)\ +\ Eu(III))} = 0$, 0.05, 0.32, 0.72, 1.2, 2.0, 2.4 and 2.8 μg·mL^{-1}; $C_{FCV} = 5.6 \times 10^{-6}$ mol·L^{-1}; pH = 3.6) Figure has been reprinted with permission from [Journal of Analytical Science. 2, 38-42 (2015)]. Copyright [2015], In Chinese

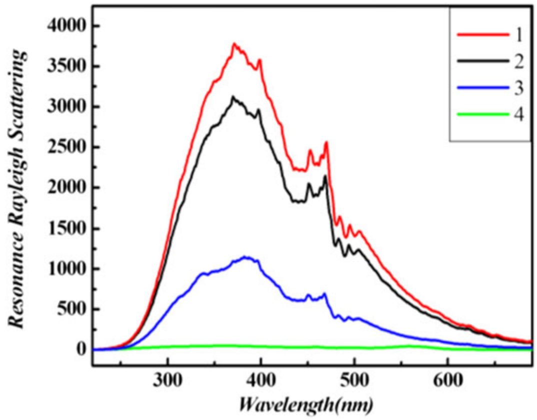

FIGURE 8 RRS spectra of the reaction system NALC-CdTe QDs (curve 4), Cu^{2+}-modulated NALC-CdTe QDs in the presence of D-Phe (curve 3) and L-Phe (curve 2), Cu^{2+}-modulated NALC-CdTe QDs (curve 1) (QDs: 1.425×10^{-4} mol·L^{-1}; Cu^{2+}: 15 μg·mL^{-1}; D-Phe: 60 μg·mL^{-1}; L-Phe: 60 μg·mL^{-1}; 1 mL PBS, pH = 7.2) Figure has been reprinted with permission from [Spectrochimica Acta Part A Molecular and Biomolecular Spectroscopy. 151, 591-597 (2015)]. Copyright [2015]

Example 5. Cu^{2+} functionalized *N*-acetyl-L-cysteine-capped CdTe quantum dots as a novel RRS probe for the recognition of phenylalanine enantiomers

In PBS solution (pH 7.2), the RRS intensity of *N*-acteyl-L-cysteine (NALC)/CdTe quantum dots (QDs) is very weak, although Cu^{2+} functionalized NALC/CdTe QDs have extremely high RRS intensity. The most important observations are that phenylalanine (PA) quenches the RRS intensity of Cu^{2+}-NALC/CdTe QDs, and that L-Phe and D-Phe have different degrees of influence. Based on the differences in and additivity of the RRS intensities of D-Phe and L-Phe, an original radial measurement analysis method for the simultaneous determination of Phe enantiomers was developed using RRS spectroscopy (Figure 8).[24] The other steps are the same as steps a, b and c in Example 1.

Based on the five examples discussed above, the newly developed ‘common-origin ray’ method can be successfully used for the simultaneous determination of different chemical components in a mixture, including similar material and chiral material. All five examples used molecular spectroscopy in the characterization and a ‘common-origin ray’ as the analytical technique, thus a novel method, not seen previously in analytical chemistry textbooks, was established for the simultaneous determination of two components in spectrally overlapping mixtures.

4 | CONCLUSION

Interpretation of the ‘measurement analysis of two radials with a common-origin point’ is simple and transparent, with direct operative ability and reliable results. This method can be used to solve the problem of the simultaneous determination of two components in completely overlapping spectral mixtures, and make up for insufficiencies in analytical chemistry textbooks. This simple analysis method has found wide application in China.[25–27]

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