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Comparative study of three modified numerical spectrophotometric methods: An application on pharmaceutical ternary mixture of aspirin, atorvastatin and clopedogrel

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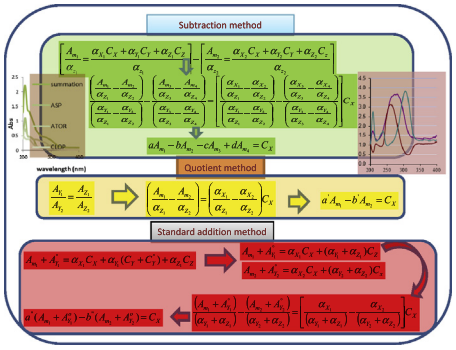
HIGHLIGHTS

- Three novel spectrophotometric methods were proposed for multi-component analysis.
- Aspirin, atorvastatin and clopedogrel were determined simultaneously.
- Subtraction method based on absorbance difference of four wavelengths.
- Quotient and standard addition were proposed.
- Mathematical explanations are illustrated and results were compared to HPLC.

GRAPHICAL ABSTRACT



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ABSTRACT

Three novel numerical methods were developed for the spectrophotometric multi-component analysis of capsules and synthetic mixtures of aspirin, atorvastatin and clopedogrel without any chemical separation. The subtraction method is based on the relationship between the difference in absorbance at four wavelengths and corresponding concentration of analyte. In this method, the linear determination ranges were 0.8–40 μg mL^{-1} aspirin, 0.8–30 μg mL^{-1} atorvastatin and 0.5–30 μg mL^{-1} clopedogrel. In the quotient method, 0.8–40 μg mL^{-1} aspirin, 0.8–30 μg mL^{-1} atorvastatin and 1.0–30 μg mL^{-1} clopedogrel were determine from spectral data at the wavelength pairs that show the same ratio of absorbance for other two species. Standard addition method was used for resolving ternary mixture of 1.0–40 μg mL^{-1} aspirin, 0.8–30 μg mL^{-1} atorvastatin and 2.0–30 μg mL^{-1} clopedogrel. The proposed methods were validated. The reproducibility and repeatability were found satisfactory which evidence was by low values of relative standard deviation (<2%). Recovery was found to be in the range (99.6–100.8%). By adopting these methods, the time taken for analysis was reduced as these methods involve very limited steps. The developed methods were applied for simultaneous analysis of aspirin, atorvastatin and clopedogrel in capsule dosage forms and results were in good concordance with alternative liquid chromatography.

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Introduction

Aspirin [ASP] is used as an analgesic, antipyretic, anti-inflammatory and antithrombic agent [1]. Atorvastatin calcium (ATOR) is an inhibitor of 3-hydroxy-3-methylglutaryl Coenzyme A (HMG-CoA) reductase. This enzyme catalyses the conversion of HMG-CoA to mevalonate, an early and rate limiting step in cholesterol biosynthesis [2]. Clopidogrel bisulphate (CLOP) is an ADP antagonist. It is used as an antithrombic agent [3]. Combined dosage forms of ASP, ATOR and CLOP are available in the market. Clinical trials showed that combination therapy when used in dyslipdaemic patient with coronary heart diseases reduced cardiovascular events. Therefore, the analysis of ternary mixture of ASP, ATOR and CLOP is very important.

The official monographs describe in procedure for individual assay of ASP [4,5], CLOP [4] and ATOR [5–7]. Literature survey reveal very few analytical methods such as spectrophotometry [8,9], inverse least squares [9], HPTLC [10] and HPLC [11,12] have been reported for the simultaneous determination of ASP, CLOP and ATOR in the ternary mixture. However, the liquid chromatography methods suffered from extraction procedure and long chromatographic analysis time. On the other hand, the inverse least squares procedures are mathematically complex-so much so that some analysts view them as black boxes and tend to avoid them [13]. The main disadvantage derivative spectrophotometry is its low reproducibility [14]. So the application of this technique required careful selection the mathematical parameters. The double divisor-ratio spectra derivative method [15–17] also cannot be popularized, because it can only be used for the mixtures that the ratio of the concentration of two interfering compounds is known.

In this paper a simple and novel three numerical spectrophotometric methods were developed for the simultaneous determination of ternary mixture, without prior separation steps. The mathematical explanation of the three procedures was illustrated. The new methods had the advantages of minimal data processing and wider range of application over the previously mentioned methods. The methods were successfully applied for the simultaneous determination of ASP, CLOP and ATOR in their ternary mixture. Furthermore, HPLC as an alternative method was applied for the resolution of the above mentioned ternary mixture.

Theory of the three novel methods

Theory of subtraction method

Consider a mixture of three compounds *X*, *Y* and *Z*. If there is no interaction among the compounds and Beer's law is obeyed for each compound, then

$$A_{m_i} = \alpha_{x_i} C_x + \alpha_{y_i} C_y + \alpha_{z_i} C_z$$

where subscript *i* refers to wavelength (i = 1, 2, 3, ..., n), A_m is the absorbance of the mixture, α_X, α_Y and α_Z are the absorptivity of *X*, *Y* and *Z* and C_X, C_Y and C_Z are the concentration of *X*, *Y* and *Z*, respectively. At any four different wavelengths where no interaction among the compounds and good linearity is present at each wavelength individually, the following equations will be obtained:

$$A_{m_1} = \alpha_{X_1} C_X + \alpha_{Y_1} C_Y + \alpha_{Z_1} C_Z \quad (1)$$

$$A_{m_2} = \alpha_{X_2} C_X + \alpha_{Y_2} C_Y + \alpha_{Z_2} C_Z \quad (2)$$

$$A_{m_3} = \alpha_{X_3} C_X + \alpha_{Y_3} C_Y + \alpha_{Z_3} C_Z \quad (3)$$

$$A_{m_4} = \alpha_{X_4} C_X + \alpha_{Y_4} C_Y + \alpha_{Z_4} C_Z \quad (4)$$

By dividing Eq. (1) by α_{z_1}, Eq. (2) by α_{z_2}, Eq. (3) by α_{z_3} and Eq. (4) by α_{z_4} and subtracting (1)–(4), the following equations will be obtained:

$$\left(\frac{A_{m_1}}{\alpha_{Z_1}} - \frac{A_{m_2}}{\alpha_{Z_2}}\right) = \left(\frac{\alpha_{X_1}}{\alpha_{Z_1}} - \frac{\alpha_{X_2}}{\alpha_{Z_2}}\right) C_X + \left(\frac{\alpha_{Y_1}}{\alpha_{Z_1}} - \frac{\alpha_{Y_2}}{\alpha_{Z_2}}\right) C_Y \quad (5)$$

$$\left(\frac{A_{m_3}}{\alpha_{Z_3}} - \frac{A_{m_4}}{\alpha_{Z_4}}\right) = \left(\frac{\alpha_{X_3}}{\alpha_{Z_3}} - \frac{\alpha_{X_4}}{\alpha_{Z_4}}\right) C_X + \left(\frac{\alpha_{Y_3}}{\alpha_{Z_3}} - \frac{\alpha_{Y_4}}{\alpha_{Z_4}}\right) C_Y \quad (6)$$

In the same way, by dividing and subtracting, Eq. (7) can be rewritten in the following way

$$\frac{\left(\frac{A_{m_1}}{\alpha_{Z_1}} - \frac{A_{m_2}}{\alpha_{Z_2}}\right)}{\left(\frac{\alpha_{Y_1}}{\alpha_{Z_1}} - \frac{\alpha_{Y_2}}{\alpha_{Z_2}}\right)} - \frac{\left(\frac{A_{m_3}}{\alpha_{Z_3}} - \frac{A_{m_4}}{\alpha_{Z_4}}\right)}{\left(\frac{\alpha_{Y_3}}{\alpha_{Z_3}} - \frac{\alpha_{Y_4}}{\alpha_{Z_4}}\right)} = \left[\frac{\left(\frac{\alpha_{X_1}}{\alpha_{Z_1}} - \frac{\alpha_{X_2}}{\alpha_{Z_2}}\right)}{\left(\frac{\alpha_{Y_1}}{\alpha_{Z_1}} - \frac{\alpha_{Y_2}}{\alpha_{Z_2}}\right)} - \frac{\left(\frac{\alpha_{X_3}}{\alpha_{Z_3}} - \frac{\alpha_{X_4}}{\alpha_{Z_4}}\right)}{\left(\frac{\alpha_{Y_3}}{\alpha_{Z_3}} - \frac{\alpha_{Y_4}}{\alpha_{Z_4}}\right)}\right] C_X \quad (7)$$

Finally:

$$aA_{m_1} - bA_{m_2} - cA_{m_3} + dA_{m_4} = C_X \quad (8)$$

where *a*, *b*, *c* and *d* are constant values presented in the results.

Eq. (8) is the mathematical foundation of multi-component analysis that permits the determination of concentration of each compound without interfering from the other compounds. The absorbance values at four points for samples were introduced to into Eq. (8) and then, the concentration of C_X will be calculated. C_Y and C_Z can also be determined by analogous procedures.

Theory of quotient method

The method calculates the analyte concentration (x) from spectral data at two wavelengths where the two species selected as interferents present the same absorbance relationship (quotient), therefore

$$\frac{A_{Y_1}}{A_{Y_2}} = \frac{A_{Z_1}}{A_{Z_2}}$$

$$\text{or } \frac{\alpha_{Y_1}}{\alpha_{Y_2}} = \frac{\alpha_{Z_1}}{\alpha_{Z_2}} \quad (9)$$

If Eq. (9) is substituted in Eq. (5), the following equation will be obtained:

$$\left(\frac{A_{m_1}}{\alpha_{Z_1}} - \frac{A_{m_2}}{\alpha_{Z_2}}\right) = \left(\frac{\alpha_{X_1}}{\alpha_{Z_1}} - \frac{\alpha_{X_2}}{\alpha_{Z_2}}\right) C_X \quad (10)$$

Finally:

$$a'A_{m_1} - b'A_{m_2} = C_X \quad (11)$$

where a' and b' are constant values presented in the results.

The absorbance values at two points for samples were introduced to into Eq. (11) and then, the concentration of C_X will be calculated. C_Y and C_Z can also be calculated as described for *X*.

Theory of standard addition method

This method can only be used for the mixtures that the ratio of the concentration of two interfering (*Y* and *Z*) compounds is known. In the other words, the concentration of the interferents is known. Using the addition method, Eqs. (1) and (2) will be

$$A_{m_1} + A^{\circ}_{Y_1} = \alpha_{X_1} C_X + \alpha_{Y_1}(C_Y + C^{\circ}_Y) + \alpha_{Z_1} C_Z$$

$$A_{m_2} + A^{\circ}_{Y_2} = \alpha_{X_2} C_X + \alpha_{Y_2}(C_Y + C^{\circ}_Y) + \alpha_{Z_2} C_Z$$

where $A^{\circ}_{Y_1}$ and C°_Y are the absorbance and concentration of standard solution of *Y* and taking into account that $C_Y + C^{\circ}_Y = C_Z$, then

$$A_{m_1} + A^{\circ}_{Y_1} = \alpha_{X_1} C_X + (\alpha_{Y_1} + \alpha_{Z_1}) C_Z \quad (12)$$

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