Wavelet Transform-Based UV Spectroscopy for Pharmaceutical Analysis

Erdal Dinç*1 and Zehra Yazan2

1 Department of Analytical Chemistry, Faculty of Pharmacy, Ankara University, Ankara, Turkey, 2 Department of Chemistry, Ankara University Faculty of Science, Ankara, Turkey

In research and development laboratories, chemical or pharmaceutical analysis has been carried out by evaluating sample signals obtained from instruments. However, the qualitative and quantitative determination based on raw signals may not be always possible due to sample complexity. In such cases, there is a need for powerful signal processing methodologies that can effectively process raw signals to get correct results. Wavelet transform is one of the most indispensable and popular signal processing methods currently used for noise removal, background correction, differentiation, data smoothing and filtering, data compression and separation of overlapping signals etc. This review article describes the theoretical aspects of wavelet transform (i.e., discrete, continuous and fractional) and its characteristic applications in UV spectroscopic analysis of pharmaceuticals.

Keywords: discrete wavelet transform, continuous wavelet transform, fractional wavelet transform, UV spectroscopy, pharmaceutical analysis

INTRODUCTION

In experimental studies, instruments or devices can provide signals (or graphs) in different formats e.g., spectrum, chromatogram, voltammogram, and electroferogram etc. The analysis of chemicals and pharmaceuticals in various samples is based upon the utilization of the measured signals of substances of interest. In practice, such an analysis for a multicomponent mixture may not be determined without a prior separation step due to spectral overlapping. Therefore, high performance liquid chromatography (HPLC) is one of the most commonly used techniques for quantitative estimation in the quality control of raw materials and commercial products in laboratories. In some cases, chromatographic determination could not be possible due to not only similar physicochemical behavior of analytes but also time- and solvent-consumption for optimal experimental conditions.

In practice, UV spectroscopic methods are widely used in chemical and pharmaceutical analysis. As compared to chromatographic ones, the use of spectroscopic methods provides a rapid analysis with low-cost and acceptable results. However, multicomponent analysis may not be possible with a traditional UV spectrophotometric approach due to spectral interferences of both active and inactive ingredients in samples. In some cases, derivative spectrophotometry (O’Haver and Green, 1976; O’Haver, 1979; Levillain and Fompeydie, 1986; Ragno et al., 2006) and its improved versions e.g., ratio spectra-derivative spectrophotometry (Salinas et al., 1990), ratio spectra-derivative spectrophotometry-zero crossing (Berzas Nevado et al., 1992; Dinç and Onur, 1998; Dinç, 1999), and double-divisior-ratio spectra-derivative spectrophotometry (Dinç and Onur, 1998; Dinç, 1999; Gohel et al., 2014; Shokry et al., 2014) could be used in place of...
conventional UV spectrophotometric method for analysis of binary and ternary mixtures without using a separation step. However, these spectral approaches may not always yield successful data due to severely overlapping spectral bands, spectral noise and baseline variation. Additionally, high-order differentiation of spectra may lead to spectral deterioration i.e., a decrease in signal intensity and signal-to-noise ratio. As a result, a number of mathematical manipulations (or signal processing methods) are often required to make instrumental signals more meaningful for analysis purpose.

Generally speaking, transform (i.e., Fourier, Hilbert, short-time Fourier, Wigner distribution, Radon, and wavelet) is a very suitable technique in the pre-treatment step to simplify signals. Fourier transform (FT) is the first method to modify chemical signal (Griffiths, 1977; Cooper, 1978; Griffiths and De Haseth, 1986; Ernst, 1989) with the mathematical essence such as filtering, convolution/deconvolution etc. FT analysis can localize signal in frequency domain very well, but not so much in time domain. In contrast, wavelet transform (WT) has the advantage of localizing signals both in time (position) and frequency (scale) domains, making it a preferable mathematical tool to replace FT in the study of the local property of a signal and the removal of the perturbation of measuring error in spectral analysis. Nowadays, WT is one of the most signal analysis algorithms commonly used in the different fields of chemistry and engineering, providing alternative ways or opportunities to resolve complex spectral bands or diverse data types of signals.

For readers interested in learning the general theory of wavelets, more details can be found in the literature (Mallat, 1988; Chui, 1992; Daubechies, 1992; Newland, 1993; Byrnes et al., 1994; Chui et al., 1994; Vetterli and Kovačević, 1995; Strang and Nguyen, 1996).

In the signal smoothing and de-noising of spectral peaks, the elimination of noise requires an application of appropriate filters to the raw spectral data such as some conventional signal filters Savitzky–Golay, Fourier and Kalman (Brown et al., 1994, 1996). The use of WT in signal analysis is two-fold: (i) to detect the singularities of a signal very likely caused by high-frequency noise and (ii) to separate the signal frequencies at different scales (Palavajhala et al., 1994; Yan-Fang, 2013; Li and Chen, 2014). To illustrate this, Barclay et al. (1997) performed a comparative study in de-noising and smoothing of Gaussian peak by using wavelet, Fourier and Savitzky–Golay filters i.e., smoothing eliminates high-frequency components of the transformed signal irrespective of their amplitudes, while de-noising eliminates small-amplitude components of the transformed signal irrespective of their frequencies.

Historically, WT principal applications in chemistry were first explored by Walczak and Massart (1997a), who presented an approach based on the application of wavelet packet transform (WPT) to the best-basis selection for the compression and de-noising of a set of signals in time-frequency domain. In their paper, the proposed technique was compared to Wickerhauser's approach (Wickerhauser, 1994) of fast approximate principal component analysis (PCA). These authors also published two more papers on the application of wavelets for data processing i.e., the introduction of WPT for noise suppression and signal compression (Walczak and Massart, 1997b) and the use of WT for signal compression and denoising, image processing, data compression and multivariate data modeling in analytical chemistry (Walczak and Massart, 1997c). On the other hand, Alberg et al. (1997) tried to introduce WT to chemometricians by suggesting the short-time FT technique as a resolution to obtain information about frequency changes over time as well as the WT for de-noising, baseline removal, determination of derivative zero crossings and signal compression. In 1997, WT application in chemical analysis was also confirmed by Wang et al. (1997) and Depczynski et al. (1997). Up to date, WT processing of the different types of raw signals has been reported for liquid chromatography (Shao et al., 1997, 1998a,b,c) and NMR spectroscopy (Neue, 1996; Barache et al., 1997), Raman spectra (Cai et al., 2001; Ehrentreich and Summchen, 2001), and voltammetry (Chen et al., 1996; Fang and Chen, 1997; Zheng et al., 1998; Zhong et al., 1998; Aballe et al., 1999; Zheng and Mo, 1999) IR and Raman spectroscopy (Shao and Huang, 2004; Hwang et al., 2005; Chalus et al., 2007; Jun-fang et al., 2007; Lai et al., 2011). In this context, as in the various fields of mathematics and engineering, the implementations of WT in analytical chemistry and neighbor disciplines has become increasingly attractive as an alternative way to analyze complex mixtures previously unresolved by traditional analytical techniques.

With reference to the above-mentioned review, the aim of this paper is to describe the fundamentals of WT methodologies and its typical implementations for UV spectroscopic analysis of pharmaceuticals.

**BRIEF HISTORY OF WAVELETS**

In the literature, the first study was related to the Haar Wavelet transform. This family was suggested by the mathematician Alfred Haar in 1909. However, the word “wavelet” was not used in the period of Haar. In fact, the word “wavelet” was invented by Morlet and the physicist Alex Grossman in 1984. After the first orthogonal Haar wavelet, the second orthogonal wavelet known as “Meyer wavelet” was formulated by the mathematician Yves Meyer in 1985. In 1988, Stephane Mallat and Meyer elaborated the concept of multiresolution. In the same year, a systematical method to construct compactly supported continuous wavelets was found by Ingrid Daubechies. Afterwards, Mallat proposed the fast wavelet transform. The emergence of this algorithm increased the implementations of the WT in the signal processing field.

In other words, the history of the wavelet families could be given in the following chronological order: Haar families in 1910, Morlet wavelet concept in 1981, Morlet and Grossman, “wavelet” in 1984, Meyer, “orthogonal wavelet” in 1985, Mallat and Meyer, multiresolution analysis in 1988, Daubechies, compact support orthogonal wavelet in 1988 and Mallat, fast wavelet transform in 1989 (c.f. Chun-Lin, 2010).

Basically, WT can be mainly classified into discrete wavelet transform (DWT) and continuous wavelet transform (CWT) in
the signal analysis. The theory and implementations of wavelets in chemistry and related fields were well documented as review papers (Leung et al., 1998; Dinç and Baleanu, 2007b; Dinç, 2013; Li and Chen, 2014; Medhat, 2015) and reference books (Walczak and Massart, 2000a,b; Walczak and Radomski, 2000; Brereton, 2003, 2008; Chau et al., 2004; Danzer, 2007; Mark and Workman, 2007; Dubrovkin, 2018).

**WAVELET TRANSFORM ALGORITHMS**

FT is based upon the decomposition of a signal into a set of trigonometric (sine and cosine) functions i.e., FT represents a signal in terms of sinusoids. The representation of FT of a signal from time mode to frequency mode is illustrated in Figure 1. For the determination of a local information in the FT, it is required to use an analyzing function $\psi$ having localization properties in both frequency and time domains. This $\psi$ function is named as a wavelet and it must be wave of finite duration.

WT contains the decomposition of a signal into a set of basic functions (wavelets). Basis functions of WT are small waves detected in different times. On the contrary to FT, WT gives information on both time and frequency, making it as an alternative approach to eliminate the resolution problem in signal analysis.

By definition, wavelets are the mathematical methods that convert the data into various coefficients and then analyze each coefficient at a resolution corresponding to its scale. Projection of a signal onto wavelet basic functions is called the wavelet transform. In other words, wavelets are mathematical functions generated from a mother wavelet $\psi(x)$ by the scaling parameter (dilation) and shifting parameter (translation) i.e., the signal is expanded on a set of the dilation (scaling parameter) of functions

$$\psi \left( \frac{x - a}{b} \right)$$  \hspace{1cm} (1)

The scaling parameter has a significant role for the variation of time and frequency resolution when processing the signal.

For a given mother wavelet (Daubechies, 1992) $\psi(x)$ by the scaling parameter and shifting parameter $a \psi(x)$, a set of functions expressed by $\psi_{a,b}(x)$ is obtained from the following equation.

$$\psi_{a,b}(x) = \frac{1}{\sqrt{|a|}} \psi \left( \frac{x - b}{a} \right), a \neq 0, a, b \in \mathbb{R}$$  \hspace{1cm} (2)

where $a$ is the scaling parameter, $b$ is the shifting parameter and $R$ is domain of real number. The mathematical expression of a CWT on a function $f(x)$ is given below

$$\text{CWT} [f(x); a, b] = \int_{-\infty}^{\infty} f(x)\psi^*_{a,b}(x)dx = \langle f(x), \psi_{a,b} \rangle$$  \hspace{1cm} (3)

here the superscript $*$ is related to the complex conjugate and $\langle f(x), \psi_{a,b} \rangle$ represents the inner product of function $f(x)$ onto the wavelet function $\psi_{a,b}(x)$.

The original signal can be completely reconstructed by a sampled version of the CWT. Usually, the exemplar is follows as

$$a = 2^{-m} \text{ and } b = n2^{-m}$$  \hspace{1cm} (4)

Here $a$ and $b$ denote scale and dilatation parameters, respectively, and $R$ is the real number. The expression of DWT can be given as

$$DWT = \int_{-\infty}^{+\infty} f(x) \psi^*_{m,n}(x) dt$$  \hspace{1cm} (5)

Where $\psi^*_{m,n}(X) = 2^{-m} \psi (2^{m}x - n)$ is the dilated and translated version of the mother wavelet. In the application of the DWT, only outputs from the low-pass filter are processed by WT. However, in the wavelet packet decomposition of signals, both outputs from the low-pass and high-pass filters are manipulated by WT (Strang and Nguyen, 1996). Multiresolution decomposition with wavelets is an interesting topic for signal and image analysis (Mallat, 1988; Daubechies, 1992).

Some families of wavelets with names and their coding list are illustrated in Table 1.

For signal processing, there is also another WT approach i.e., fractional wavelet transform (FWT) specifically designed for rectification of the limitations of the WT and fractional FT (Blu and Unser, 2000, 2002; Unser and Blu, 2000). FWT is based on the fractional B-splines. As it is already known, the splines play an important role on the early development of the theory of WT.

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**FIGURE 1** | Representation of Fourier transform of a signal from time domain to frequency domain.
TABLE 1 | Families of wavelets with names and their coding list.

| Wavelet families          | Coding |
|---------------------------|--------|
| Haar                      | haar   |
| Daubechies                | db     |
| Symlets                   | sym    |
| Coiflets                  | coif   |
| BiorSplines               | bior   |
| ReverseBior               | rbio   |
| Meyer                     | meyr   |
| Dmeyer                    | dmey   |
| Gaussian                  | gaus   |
| Mexican hat function      | mextx  |
| Morlet                    | morl   |
| Complex Gaussian          | cgiau  |
| Shannon                   | shan   |
| Frequency B-Spline        | fbsp   |
| Complex Morlet            | cmor   |

A B-spline is a generalization of the Bezier curve. Let a vector known as the knot be defined by \( T = \{ t_0, t_1, \ldots, t_m \} \) where \( T \) is a non-decreasing sequence with \( t_i \in [0, 1] \), and define control point \( P_0, P_n \). The knots \( t_0, t_1, \ldots, t_m \) is called internal knots. If \( p = m-n \) denotes the degree, the basis function is defined as follows:

\[
N_{i,0}(t) = f(x) = \begin{cases} 
1, & \text{if } t_i \leq t < t_{i+1} \text{ and } t_{i+1} \\
0 & \text{otherwise}
\end{cases} \tag{6}
\]

and

\[
N_{i,p}(t) = \frac{t - t_i}{t_{i+p} - t_i} N_{i, p-1}(t) + \frac{t_{i+p+1} - t}{t_{i+p+1} - t_{i+1}} N_{i+1, p-1}(t) \tag{7}
\]

Therefore, the curve defined by

\[
C(t) = \sum_{i=0}^{n} P_i N_{i,p}(t) \tag{8}
\]

is a B-spline.

Fractional B-spline: The fractional B-spline is defined as

\[
\beta^\alpha_+(x) = \sum_{k=0}^{\infty} (-1)^k \binom{\alpha + 1}{k} (x - k)^\alpha \quad \frac{\Gamma(\alpha + 1)}{\Gamma(k + 1)(\alpha - k + 1)} \tag{9}
\]

where Euler's Gamma function is obtained by

\[
\Gamma(\alpha + 1) = \int_0^{+\alpha} x^\alpha e^{-x} \, dx \tag{10}
\]

and

\[
(x - k)^\alpha = \max(x - k, 0)^\alpha \tag{11}
\]

The forward fractional finite difference operator of order \( \alpha \) is defined as

\[
\Delta_+^\alpha f(x) = \sum_{k=0}^{\infty} (-1)^k \binom{\alpha}{k} f(x - k) \tag{12}
\]

where

\[
\binom{\alpha}{k} = \frac{\Gamma(\alpha + 1)}{\Gamma(k + 1)(\alpha - k + 1)} \tag{13}
\]

B-splines fulfill the convolution property, namely

\[
\beta^\alpha_+ \ast \beta^\alpha_+ = \beta^\alpha_+ \tag{14}
\]

The centered fractional B-splines of degree \( \alpha \) is defined as

\[
\beta^\alpha_c(x) = \frac{1}{\Gamma(\alpha + 1)} \sum_{k \in \mathbb{Z}} (-1)^k \binom{\alpha + 1}{k} |x - k|^\alpha \tag{15}
\]

where

\[
|x|^\alpha = \begin{cases}
\frac{|x|^{\alpha}}{-\sin(\pi \alpha)}, & \alpha \text{ not even} \\
\frac{x \log x \pi}{(-1)^{1+n} \pi}, & \alpha \text{ even}
\end{cases} \tag{16}
\]

The fractional B-spline wavelet is defined as

\[
\psi^\alpha_\frac{x}{2} = \sum_{k \in \mathbb{Z}} (-1)^k \frac{\alpha}{2^\alpha} \sum_{m \in \mathbb{Z}} \left( \frac{\alpha + 1}{1} \right) \beta^\alpha_+(1 + k - 1) \beta^\alpha_+(x - k) \tag{17}
\]

We mention that the fractional splines wavelets of degree obey the following

\[
\int_{-\infty}^{+\infty} X^n \psi^\alpha_\frac{x}{2} \, dx = 0, \ldots, [\alpha] \tag{18}
\]

and the Fourier transform fulfills the following relations

\[
\hat{\psi}^\alpha_\frac{\alpha}{2} (\alpha \sigma) = C(\alpha \sigma)^{\alpha+1}, \text{ as } \sigma \to 0 \tag{19}
\]

and

\[
\hat{\psi}^\alpha_\frac{\alpha}{2} (\alpha \sigma) = C(\alpha \sigma)^{\alpha+1}, \text{ as } \sigma \to 0 \tag{20}
\]

where \( \hat{\psi}^\alpha_\frac{\alpha}{2} (\alpha \sigma) \) is symmetric. The fractional spline wavelet behaves like a fractional derivative operator.

**STRATEGIES IN CWT APPLICATIONS TO UV SPECTROSCOPY ANALYSIS OF MULTICOMPONENT MIXTURES**

For the past 15 years, the potential application of CWT in chemistry, especially in combination with other mathematical methods, leads us to a conclusion that WT has interestingly became a useful algorithm for UV quantitative analysis of pharmaceuticals. Four different models (i.e., continuous wavelet transform-zero crossing (CWT-ZC), ratio spectra-continuous wavelet transform (RS-CWT), ratio spectra-continuous wavelet transform-zero crossing (RS-CWT-ZC), and double divisor ratio spectra-continuous wavelet transform (DDRS-CWT)) were described in the implementation of CWT to UV spectroscopic data for the resolution of overlapping spectra to quantify drugs.
in different types of samples. The modeling of CWT—UV spectroscopic approaches are detailed below. Fundamentally, these approached can be successfully applied to the UV spectroscopic analysis of binary and ternary mixtures, provided that the law of additivity of absorbance is obeyed.

CONTINUOUS WAVELET TRANSFORM-ZERO CROSSING

The application of CWT-ZC approach to UV spectroscopic signals was first proposed by Dinç and Baleanu (2003a).

If a mixture of two analytes (M and N) is considered (see Figure 2A) and the absorbance of this binary mixture is measured at λ\textsubscript{i}, we can have the following equation (Charlotte Grinter and Threlfall, 1992):

\[ A_{\text{mix}, \lambda_i} = \alpha_{M, \lambda_i}C_M + \beta_{N, \lambda_i}C_N \]  

(21)

where \( A_{\lambda_i} \) is the absorbance of the binary mixture at wavelength \( \lambda_i \), and the coefficients are the absorptivities of M and N, respectively. \( C_M \) and \( C_N \) represent the concentrations of M and N, respectively.

If CWT is applied to Equation (21), the following function can be obtained as

\[ \psi_{(a.b), \text{MIX}, \lambda_i} = \psi_{(a.b), M, \lambda_i}C_M + \psi_{(a.b), N, \lambda_i}C_N \]  

(22)

If \( \psi_{(a.b), N, \lambda_i}C_N = 0 \), then we obtain the following equation

\[ \psi_{(a.b), \text{MIX}, \lambda_i} = \psi_{(a.b), M, \lambda_i}C_M \]  

(23)

Equation (23) shows that CWT (\( \psi_{(a.b), M, \lambda_i}C_M \)) amplitudes of M in the binary mixture are dependent only on \( C_M \) regardless of \( C_N \) (see Figure 2B).

RATIO SPECTRA-CONTINUOUS WAVELET TRANSFORM

Apart from CWT-ZC approach, overlapping spectral bands in a binary mixture could be solved by the application of a combined hybrid approach i.e., RS-CWT (Dinç and Baleanu, 2004a,c).

The absorption spectra of M and N compounds, and their mixture are indicated in Figure 3A. By being divided by the standard spectrum (\( A_{N, \lambda_i} = \beta_{N, \lambda_i}C_N^0 \)) of one of the compounds in the binary mixture, Equation (21) becomes

\[ \frac{A_{m, \lambda_i}}{\beta_{\lambda_i}C_N^0} = \frac{\alpha_{M, \lambda_i}C_M}{\beta_{\lambda_i}C_N^0} + \frac{\beta_{N, \lambda_i}C_N}{\beta_{\lambda_i}C_N^0} \]  

(24)

Figure 3B shows the ratio spectra of analytes and their binary mixture. If CWT is applied to Equation (24), the following equation can be obtained

\[ \text{CWT} \left[ \frac{A_{m, \lambda_i}}{\beta_{\lambda_i}C_N^0} \right] = \text{CWT} \left[ \frac{\alpha_{M, \lambda_i}}{\beta_{\lambda_i}} \frac{C_M}{C_N^0} \right] + \text{CWT} \left[ \frac{\beta_{N, \lambda_i}}{\beta_{\lambda_i}} \frac{C_N}{C_N^0} \right] \]  

(25)

If \( \frac{\beta_{N, \lambda_i}}{\beta_{\lambda_i}} \) \( \frac{C_N}{C_N^0} = 0 \), then we obtain

\[ \text{CWT} \left[ \frac{A_{m, \lambda_i}}{\beta_{\lambda_i}C_N^0} \right] = \text{CWT} \left[ \frac{\alpha_{M, \lambda_i}}{\beta_{\lambda_i}} \frac{C_M}{C_N^0} \right] \]  

(26)

The ratio-CWT amplitudes of the binary mixture given in Equation (26) depend only on \( C_M \) and \( C_N^0 \) regardless of \( C_N \) (see Figure 3C).

RATIO SPECTRA-CONTINUOUS WAVELET TRANSFORM-ZERO CROSSING

In RS-CWT-ZC approach (Dinç et al., 2005a), if a mixture of three analytes (X, Y, and Z) is considered and the absorbance of this ternary mixture is measured at \( \lambda_i \), the following mathematical expression (Charlotte Grinter and Threlfall, 1992) would be given

\[ A_{\text{mix}, \lambda_i} = \alpha_{X, \lambda_i}C_X + \beta_{Y, \lambda_i}C_Y + \gamma_{Z, \lambda_i}C_Z \]  

(27)
Where $A_{\text{mix}, \lambda, i}$ is the absorbance of the ternary mixture at wavelength $\lambda_{i}$, and coefficients $\alpha_{X, \lambda, i}$, $\beta_{Y, \lambda, i}$, and $\gamma_{Z, \lambda, i}$ denote the absorptivities of X, Y, and Z, respectively. $C_{X}$, $C_{Y}$, and $C_{Z}$ represent the concentrations of X, Y, and Z, respectively.

If Equation (27) is divided by the spectrum of a standard solution ($C_{X}^{0}$) of one of the compounds in the ternary mixture, we have the following equation:

$$A_{\text{mix}, \lambda, i}^{0} = \frac{\alpha_{X, \lambda, i} C_{X}^{0}}{\alpha_{X, \lambda, i} C_{X}^{0} + \beta_{Y, \lambda, i} C_{Y}^{0} + \gamma_{Z, \lambda, i} C_{Z}^{0}}$$  \hspace{1cm} (28)

If CWT is applied to Equation (28), the following equation can be obtained

$$\text{CWT} \left[ \frac{A_{\text{mix}, \lambda, i}}{\alpha_{X, \lambda, i} C_{X}^{0}} \right] = \text{CWT} \left[ \frac{\beta_{Y, \lambda, i} C_{Y}^{0}}{\alpha_{X, \lambda, i} C_{X}^{0}} \right] + \text{CWT} \left[ \frac{\gamma_{Z, \lambda, i} C_{Z}^{0}}{\alpha_{X, \lambda, i} C_{X}^{0}} \right] \hspace{1cm} (29)$$

Equation (29) indicates that the CWT amplitudes of the ratio spectra of the ternary mixture are dependent only on $C_{Z}$ and $C_{X}^{0}$ regardless of the concentrations of other compounds.

### DOUBLE DIVISOR RATIO SPECTRA–CONTINUOUS WAVELET TRANSFORM

In addition to RS-CWT-ZC approach, the spectral resolution of ternary mixtures could be effectively done by DDRS-CWT approach (Dinç and Baleanu, 2008a) as follows.

When two compounds in the ternary mixture is used as a double divisor, we have

$$A_{\text{mix}, \lambda, i}^{0} = \alpha_{X, \lambda, i} C_{X}^{0} + \beta_{Y, \lambda, i} C_{Y}^{0} \hspace{1cm} (30)$$

By dividing Equation (27) and (30), we obtain as follows

$$\frac{A_{\text{mix}, \lambda, i}}{\alpha_{X, \lambda, i} C_{X}^{0} + \beta_{Y, \lambda, i} C_{Y}^{0}} = \frac{\alpha_{X, \lambda, i} C_{X}}{\alpha_{X, \lambda, i} C_{X}^{0} + \beta_{Y, \lambda, i} C_{Y}^{0} + \gamma_{Z, \lambda, i} C_{Z}} \hspace{1cm} (31)$$
| Pharmaceuticals | Method | Wavelet Families | Type of data | References |
|------------------|--------|-----------------|--------------|------------|
| Thiamine HCl, pyridoxine HCl | CWT-zero crossing | Daubechies, Biorthogonal | UV absorption spectra | Dinç and Baleanu, 2003a |
| Hydrochlorothiazide, spironolactone | CWT-zero crossing | Daubechies, Biorthogonal | UV absorption spectra | Dinç et al., 2003 |
| Thiamine HCl, pyridoxine HCl | CWT-zero crossing | Mexican hat function, Meyer | UV absorption spectra | Dinç and Baleanu, 2003b |
| Thiamine HCl, pyridoxine HCl | CWT-zero crossing | Gaussian1, Gaussian2 | UV absorption spectra | Dinç and Baleanu, 2004a |
| Caffeine, propyphenazone | DWT-CWT-zero crossing | Mexican and Haar | UV absorption spectra | Dinç et al., 2004a |
| Benazepril, hydrochlorothiazide | DWT-CWT-zero crossing | Coiflets2 and Gaussian2 | UV absorption spectra | Dinç et al., 2004b |
| Hydrochlorothiazide, Spironolactone | CWT-zero crossing | Haar, Mexican hat function | UV absorption spectra | Dinç and Baleanu, 2004c |
| Benazepril, hydrochlorothiazide | CWT-zero crossing | Mexican, Haar, Daubechies3 | UV absorption spectra | Dinç et al., 2005b |
| Ascorbic acid, acetylsalicylic acid | CWT-zero crossing | Reverse Biorthogonal | UV absorption spectra | Dinç et al., 2005c |
| Diminazene acetate and phenazine | CWT-zero crossing | Mexican hat wavelet function | UV absorption spectra | Dinç and Baleanu, 2007a |
| Quinapril, hydrochlorothiazide | CWT-zero crossing | Mexican hat function | UV absorption spectra | Dinç and Baleanu, 2007b |
| Oxfendazole and oxyclozanide | CWT-zero crossing | Symlets | UV absorption spectra | Dinç et al., 2007d |
| Levodopa, benserazide | CWT-zero crossing | Coiflets | UV absorption spectra | Dinç et al., 2007c |
| Chlortetracycline, benzoic acid | CWT-zero crossing | Mexican hat function | UV absorption spectra | Dinç et al., 2007c |
| Pyridoxine hydrochloride, isoniazide | CWT-zero crossing | Morlet, Biorthogonal | UV absorption spectra | Dinç et al., 2009a |
| Risedronate sodium | CWT-zero crossing | Mexican hat function, Symlets | UV absorption spectra | Dinç et al., 2009a |
| Ampicillin sodium, sulbactam sodium | CWT-zero crossing | Mexican hat function, Daubechies, Symlets, Coiflets, Biorthogonal, Gaussian | UV absorption spectra | Dinç et al., 2009a |
| Paracetamol, chloroxoxide | CWT-zero crossing | Biorthogonal | UV absorption spectra | Dinç et al., 2009b |
| Levasirole, triclabendazole | CWT-zero crossing | Gaussian, Biorthogonal | UV absorption spectra | Dinç et al., 2009b |
| Telmisartan, hydrochlorothiazide | CWT-zero crossing | Haar and Biorthogonal1.5 | UV absorption spectra | Dinç and Baleanu, 2010a |
| Perindopril, indapamide | CWT-zero crossing | Daubechies, Meyer | UV absorption spectra | Sohrabi et al., 2011 |
| Valsartan, amiodipine | DWT-CWT-zero crossing | Daubechies, Reverse Biorthogonal, Gaussian | UV absorption spectra | Dinç et al., 2011b |
| Metformin hydrochloride, glibenclamide | CWT-zero crossing | Biorthogonal, Coiflets, Daubechies, Hair | UV absorption spectra | Dinç et al., 2013a |
| Trimethoprim, sulphonamethoxazole | CWT-zero crossing | Mexican hat function | UV absorption spectra | Shariat-Rad et al., 2012 |
| Amiodipine, atorvastatin | CWT-zero crossing | Symlets | UV absorption spectra | Dinç et al., 2015b |
| Estradiol valerate, cyproterone acetate | CWT-zero crossing | Mexican hat function, Daubechies, Biorthogonal | UV absorption spectra | Devrim et al., 2014 |
| Lamivudine, zidovudine | CWT-zero crossing | Mexican hat wavelet, Symlets, Daubechies | UV absorption spectra | Dinç et al., 2013b |
| Diphenhydramine hydrochloride | CWT-zero crossing | Biorthogonal | UV absorption spectra | Darwish et al., 2014 |
| Ambroxol hydrochloride, doxycycline | CWT-zero crossing | Haar wavelet function | UV absorption spectra | Dinç et al., 2015 |
| Oxfendazole, oxyclozanide | MOFrFT-CWT-zero crossing | Mexican hat | UV absorption spectra | Dinç et al., 2017b |
| Atenolol, chlorothalidone | CWT-zero crossing | Coiflet, Mexican Hat function | UV absorption spectra | Dinç et al., 2017b |
| Valsartan, hydrochlorothiazide | CWT-zero crossing | Mexican hat function, Daubechies | UV absorption spectra | Dinç et al., 2017b |
Equation (31) can be simplified to
\[
\frac{A_{mix, \lambda_i}}{\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o} = k + \frac{\gamma_{Z, \lambda_i}C_{Z}}{\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o} \tag{32}
\]

Where \( k = \frac{\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o}{\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o} \) represents a constant for a given concentration range with respect to \( \lambda_i \) in a certain region or point of wavelength.

A typical case is when \( C_{X}^o \) and \( C_{Y}^o \) are the same or very close to each other, namely \( C_{X}^o = C_{Y}^o \) or \( \equiv C_{X}^o \equiv C_{Y}^o \). Therefore, we obtain
\[
\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o = C_{X}^o (\alpha_{X, \lambda_i} + \beta_{Y, \lambda_i}) \tag{33}
\]

and Equation (32) can be written as
\[
\frac{A_{mix, \lambda_i}}{\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o} = k + \frac{\gamma_{Z, \lambda_i}C_{Z}}{C_{X}^o (\alpha_{X, \lambda_i} + \beta_{Y, \lambda_i})} \tag{34}
\]

After applying CWT to Equation (31), we have
\[
\text{CWT}_{(a,b)} \left( \frac{A_{mix, \lambda_i}}{\alpha_{X, \lambda_i}C_{X}^o + \beta_{Y, \lambda_i}C_{Y}^o} \right) \frac{1}{C_{X}^o} = \text{CWT}_{(a,b)} \left( \frac{\gamma_{Z, \lambda_i}C_{Z}}{\alpha_{X, \lambda_i} + \beta_{Y, \lambda_i}} \right) \frac{1}{C_{X}^o} \tag{35}
\]
or
\[
\text{CWT}_{(a,b)} \left( \frac{A_{mix, \lambda_i}}{\alpha_{X, \lambda_i} + \beta_{Y, \lambda_i}} \right) = \text{CWT}_{(a,b)} \left( \frac{\gamma_{Z, \lambda_i}C_{Z}}{\alpha_{X, \lambda_i} + \beta_{Y, \lambda_i}} \right) \tag{36}
\]

In Equation (36), \( C_{Z} \) is to proportional to the coefficients, \( \text{CWT}_{(a,b)} \left( \frac{A_{mix, \lambda_i}}{\alpha_{X, \lambda_i} + \beta_{Y, \lambda_i}} \right) \), at \( \lambda_i \). If this procedure is separately applied for pure \( Z \) and its ternary mixture, the \( \text{CWT}_{(a,b)} \) coefficients are coincided at some characteristic point or region of wavelength, independent upon both \( C_{X} \) and \( C_{Y} \).

**WAVELET TRANSFORM-BASED UV SPECTROSCOPIC ANALYSIS OF PHARMACEUTICALS**

Typical applications of CWT and FWT algorithms for UV spectroscopic analysis of pharmaceuticals are displayed in Tables 2–5. It is worth mentioning that WT could be solely applied to raw spectra and ratio spectra (as above-specified) as well as utilized as a hybrid approach (FWT-derivative, FWT-CWT-zero crossing, WT combined with multivariate calibration) for the simultaneous determination of analytes in pharmaceutical binary and ternary mixtures. It was shown that wavelet analysis of UV spectroscopic data was performed by using Wavelet Toolbox and m-file in MATLAB software. The numerous works provided by Dinç and co-workers have clearly highlighted the success of WT-based UV spectroscopic analysis for multicomponent synthetic mixtures, veterinary and pharmaceutical dosage forms as well as different types of test (e.g., assay, in vitro dissolution, stability indicating). Most studies proved it to be suitable for the routine analysis of dosage forms with good precision and accuracy, comparable to HPLC.

**CONCLUSIONS**

In the point of view of UV spectroscopic analysis of multicomponent mixtures, CWT-based UV spectroscopic
methods have outperformed both conventional and derivative UV spectroscopy in resolving spectrally binary and ternary mixtures. Nevertheless, wavelet analysis may not also have a sufficient power to resolve overlapping spectra of analytes in samples due to similarity of molecular structures and signal frequencies in some cases. They may not give desirable results for a complex mixture containing more than three compounds and/or a significant difference in ratios of active ingredients. In such a case, the use of WT coupled with chemometric PLS and PCR calibrations is advisable. Undoubtedly, however, wavelets can still be used as a mathematical prism for signal analysis because they can offer many possibilities such as baseline correction, noise removal and resolution of overlapping peaks, when the frequencies of analyzed components are significantly different from each other.

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Contributions of ED are planning and writing of the review paper. Contributions of ZY are literature review, collection, editing, and format arrangement.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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