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Evaluation of the efficiency of continuous wavelet transform as processing and preprocessing algorithm for resolution of overlapped signals in univariate and multivariate regression analyses; an application to ternary and quaternary mixtures

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ABSTRACT

Wavelets have been adapted for a vast number of signal-processing applications due to the amount of information that can be extracted from a signal. In this work, a comparative study on the efficiency of continuous wavelet transform (CWT) as a signal processing tool in univariate regression and a pre-processing tool in multivariate analysis using partial least square (CWT-PLS) was conducted. These were applied to complex spectral signals of ternary and quaternary mixtures. CWT-PLS method succeeded in the simultaneous determination of a quaternary mixture of drotaverine (DRO), caffeine (CAF), paracetamol (PAR) and *p*-aminophenol (PAP, the major impurity of paracetamol). While, the univariate CWT failed to simultaneously determine the quaternary mixture components and was able to determine only PAR and PAP, the ternary mixtures of DRO, CAF, and PAR and CAF, PAR, and PAP. During the calculations of CWT, different wavelet families were tested. The univariate CWT method was validated according to the ICH guidelines. While for the development of the CWT-PLS model a calibration set was prepared by means of an orthogonal experimental design and their absorption spectra were recorded and processed by CWT. The CWT-PLS model was constructed by regression between the wavelet coefficients and concentration matrices and validation was performed by both cross validation and external validation sets. Both methods were successfully applied for determination of the studied drugs in pharmaceutical formulations.

1. Introduction

Wavelet transform (WT) is one of the recent techniques for signal processing. It is defined as mathematical functions that cut up data into different frequency components, and then study each component with a resolution matched to its scale [1]. Wavelet signal processing is different from other signal-processing methods because of the unique properties of wavelets (i.e., wavelets can be symmetric or asymmetric, sharp or smooth, regular or irregular). It can represent signals sparsely, capture the transient features of signals, and enable signal analysis at multiple resolutions. WT involves the decomposition of a signal function or vector e.g., a spectrum of a chemical species into simpler, fixed building blocks at different scales and positions [2]. Continuous wavelet transform (CWT) combined either with a zero-crossing technique [3,4] or ratio spectra [5] was used for simultaneous determination of chemical species in binary and ternary mixtures.

Although univariate methods are simple, only one data point being used for regression with the concentration while about 99.8% of the data is not used. Data collection can limit the throughput of an analytical methodology. In addition, a univariate measurement is extremely sensitive to interferents. It is often impossible to differentiate an analyte-specific signal from an interferent when looking at only one point of a data spectrum.

On the other hand, multivariate methods involve the use of the multiple data points (e.g., the response at a range of potentials or wavelengths) to be regressed with the concentration several advantages, often reducing noise and resolving interferents, so, they are generally better than univariate ones as they increase the amount of possible information that can be obtained without loss. The advantages of multivariate methods come at a cost of computational power and complexity, but these drawbacks are easily handled with common mathematical software packages [6].

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Drotaverine (DRO) is a non-anticholinergic, spasmolytic agent that has excellent smooth muscle relaxant properties [7,8]. Caffeine (CAF) is a potent stimulant of the central nervous system and has been added in various analgesic combinations to improve their analgesic efficacy [8]. Paracetamol (PAR) also known as acetaminophen is a widely used analgesic and antipyretic agent for the relief of fever, headaches and minor pains. It is a major ingredient in numerous cold and flu remedies. In combination with non-steroidal anti-inflammatory drugs and opioid analgesics; it is effective for treatment of minor, non-inflammatory conditions in patients who are prone to gastric symptoms [9,10]. *p*-Aminophenol (PAP) is the primary impurity and degradation product of PAR, and it should be tested in PAR formulations as it may present either from synthesis and/or degradation during storage [11, 12]. The quantity of PAP must be strictly controlled as it is reported to have nephrotoxic and teratogenic effects [12]. The chemical structure for each of the studied compounds is shown in Fig. 1 (a–d).

CAF and PAR are present in combination in most of common cold and analgesic preparations, so, many methods have been reported for their simultaneous determination. The most recent methods included spectrophotometry [13], chemometric [14], high performance liquid chromatography (HPLC) [15] and capillary electrophoresis [15]. The analysis of mixtures containing DRO, CAF and PAR was described in few analytical reports. These reports proposed spectrophotometric [16,17] thin layer chromatographic (TLC) [17] and HPLC [16,18–20] while for CAF, PAR in the presence of PAP was determined using chemometrics [21–23] and HPLC [24,25]. In the present study, the efficiency of CWT as processing and pre-processing in univariate and multivariate calibration methods, respectively, was developed for the purpose of quantitative spectral signal resolution of DRO, CAF, PAR and PAP in their quaternary and ternary mixtures without preliminary separation steps.

2. Theoretical Background

2.1. Continuous Wavelet Transformation (CWT)

The wavelets are scaled and translated copies of a finite length or fast-decaying oscillating waveform [26]. To overcome the problem of noisy and incomplete data, WT has been successfully put on a sound statistical basis by Donoho and Johnstone [27]. This technique has been applied effectively to de-noising [28,29], data compression [30], baseline and background correction, regression and classification, and processing of analytical images in analytical chemistry. Recently, the combined use of CWT and zero-crossing technique with a mathematical model for the resolution of multi-component overlapping signals has been formulated by Dinc and Baleanu [31,32]. The two methods of CWT and zero-crossing technique were simultaneously applied to resolution of various binary and ternary mixtures [33–36].

The main idea of WT is to represent any arbitrary function as a superposition of wavelets [37]. A wavelet is defined as a number of functions $\Psi_{a,\,b}(\lambda)$ derived from a basic function $\Psi(\lambda)$ by dilation (scale) and shift (translation). Therefore the basic function is often called a *mother wavelet* since it gives birth to a family of wavelets. There are many families of wavelet bases, e.g. Daubecies, Symlet, Coiflet, Meyer … etc.

$$\Psi a, b(\lambda) = \frac{1}{\sqrt{|a|}}\Psi\left(\frac{\lambda - b}{a}\right) \quad , \quad a \neq 0 \quad , \quad a, b \in R$$

where, a denotes the scale parameter which is a variable used to control the scaling, b represents the translation parameter controlling the translation and R is the domain of real numbers. A mother wavelet $\Psi(\lambda)$ generates the set of functions $\Psi a, b(\lambda)$ by scaling (or dilatation) and shifting (or translation).

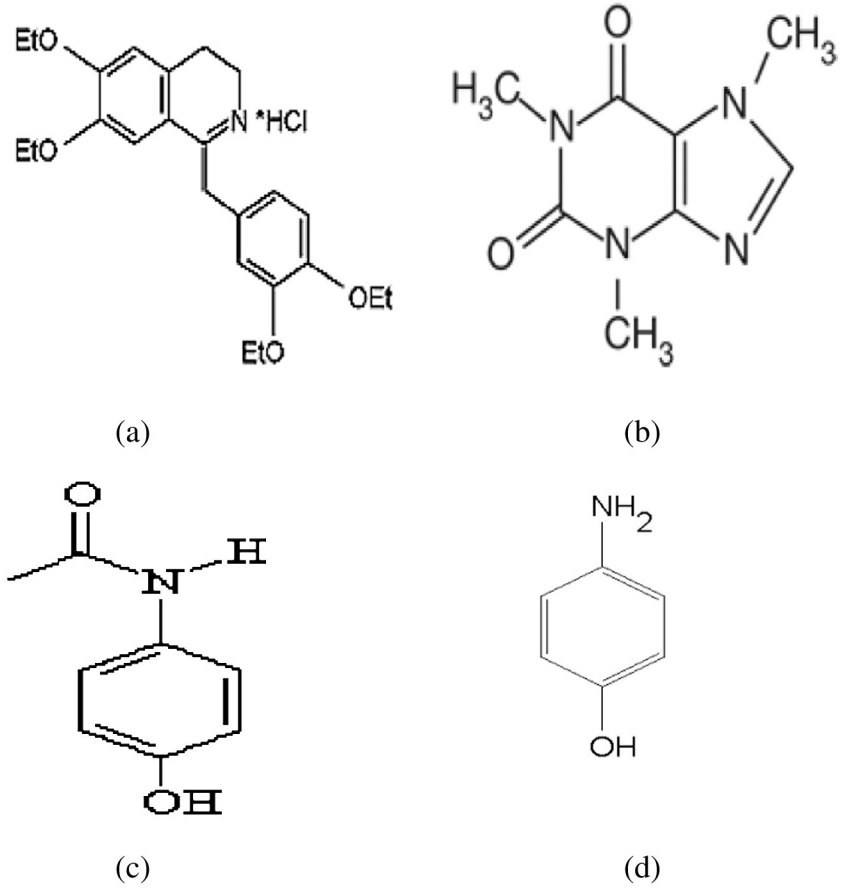

Fig. 1. Structural formulae for (a) Drotaverine, (b) Caffeine, (c) Paracetamol and (d) Para-aminophenol.