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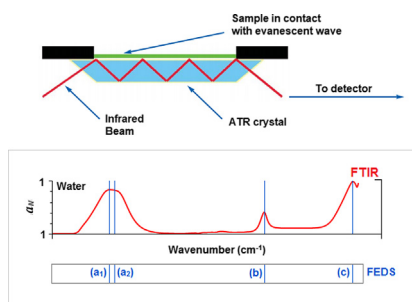
Functional transformation of Fourier-transform mid-infrared spectrum for improving spectral specificity by simple algorithm based on wavelet-like functions



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 January 2018

Revised 22 May 2018

Accepted 23 May 2018

Available online 24 May 2018

Keywords:

Derivative spectroscopy

Functional transformation

Wavelet

Infrared spectroscopy

ABSTRACT

Herein a simple algorithm for the mathematical transformation of FTIR spectrum was developed, evaluated, and applied for description of different systems. Water, ethanol, *n*-butanol, *n*-hexanol, formic acid, acetic acid, citric acid, and water-acetic acid mixtures at different concentrations were used as model systems. We found that functional transformation of FTIR spectrum can be performed by functionally-enhanced derivative spectroscopy approach using the Function P, which is defined as $P = (1 + a_j)(s)^{-0.5}$ where a_j and s are the absorbance and the scale factor, respectively. It is also demonstrated that Function P can be used for qualitative and quantitative analysis of pure substances and mixtures. It is concluded that Function P can be understood as a wavelet transformation, which is evaluated at small times and displacements, with scaling factor given by the change of absorbance inverse.

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Introduction

Infrared (IR) spectroscopy is an analytical technique, which is currently used in the study of a wide range of samples of different nature from pure substance to mixtures. However, the spectral analysis of substances, mixtures, and materials generates frequently a poorly resolved spectrum, owing to the existence of

highly overlapped and hidden peaks. Spectral signal overlapping (SSO) is produced by the finite resolution of the measuring device and causes spectral line distortion. SSO can be solved by increasing the instrumental resolution when it is not associated with intrinsic physical factors of investigated material. The SSO resulting of intrinsic factors is usually observed in spectra of materials with random structures, such as glass or aqueous systems. In addition, it is strongly characterized by fewer bands and peak broadening [1]. Therefore, interpretation not only hindered by the presence of hiding signals in mixture and by a poor molecular resolution,

Peer review under responsibility of Cairo University.

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<https://doi.org/10.1016/j.jare.2018.05.009>

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but also, some applications are seen to be limited as a result of external or internal factors (e.g., environmental humidity, water as sub-product or water as inherent constituent).

Different steps are commonly used to study the SSO by hidden and overlapped peaks; these are: (i) to collect all available information on the system under investigation, (ii) to increase the resolution by separation of overlapped peaks into their components and (iii) to make a curve fitting of the experimental spectrum by a function, which is the sum of the individual peaks [2,3]. Generally, it is widely accepted that the reliability analysis depends to a large extent on the degree of progress of these steps.

Among methods to evaluate the existence of overlapped and hidden peaks and determine their positions are: (i) spectral deconvolution [1,4–6] and (ii) spectral differentiation (or derivative spectroscopy) [7,8].

From the above, the ideal mathematical method for narrowing of an FTIR spectrum should eliminate, or at least to reduce the SSO, and this way to allow a direct estimation of the number of overlapping bands and their position, in order to achieve the separation of signals associated with different components or contributions in complex samples, and therefore, to improve the molecular specificity of spectral analysis. But also, spectral information should be keeping, or at least recovered, as far as possible, to permit the adaptability of methodology for different analytical systems. In addition, algorithms with a reduced data structure and calculation requirements ease the adaptability of computer systems applied to new technologies based on web, remote sensing or mobile operating system. In consequence, the mathematical narrowing of FTIR spectra has a significant relevance for new applications of FTIR spectroscopy as metabolomics, cellular differentiation and complex sample analysis (e.g., soil, biological fluids, biomolecules, foods and other) [9–12].

Herein a simple algorithm for the mathematical transformation of FTIR spectrum was developed, evaluated, and applied for description of different systems (pure water and water-acetic acid mixtures as model systems). These systems were selected because water and molecules with carboxylic groups are important constituents of many engineered, natural, and biological systems.

Functionally-enhanced derivative spectroscopy (FEDS): Algorithm

The “functional transformation” approach to modify data produces a code, which often faster to program, more expressive, and easier to debug and maintain than a more traditional programming [13]. By functional transformation, a set of functions define how to transform a set of structured data from its original form into another form. It is expected that transforming functions are “pure functions” and therefore these are self-contained (i.e., data can be freely ordered and rearranged without entanglement or interdependencies) and stateless (i.e., that executing of the same function or specific set of functions on the same input will always result the same output data) [13–15]. Here, a strategy based on “non-pure” functions are used because a FTIR spectrum is a data set with a fixed order in function of vibrational energy. However, transformation was based on mathematical functions and logical association defined from original data [13].

In this case, finite approximation method was used to compute the derivatives of the spectra. Usually, derivative algorithm utilizes a set of signal resolution to compute differences ($\Delta v = |v_j - v_i|$ where Δv is the separation between adjacent data). Eq. (1) showed the finite approximation of the first derivative for FTIR spectrum, which is plotted usually in function of v :

$$y' = \frac{ds}{dv} \approx \frac{\Delta s}{\Delta v} = \frac{s(v_j) - s(v_i)}{v_j - v_i} \quad (1)$$

where s and Δs denote the signal for a specific values of v and the difference between adjacent signals, respectively. For another

spectrum usually used in analytical sciences, the ultraviolet-visible spectrum, the plotting of data is typically described as a function of λ .

Function P is the algorithm proposed in this work (the name P is given by the word “primera” in Spanish). Basically, Function P can be understood as a functional transformation that contracts the signals of FTIR spectrum in function of critical points without changing the relative position of them. It is expected that this transformation could be useful from analytical point of view. The sequence of steps associated for the obtaining of Function P is:

Normalization of absorbance data (a) respect to the maximum absorbance (a_{max})

$$a_N = \frac{a}{a_{max}} \quad (2)$$

Transformation of data from a_N to a_N^{-1} , and later, to carry out the determination of derivative spectrum from values of a_N^{-1} using the finite approximation method

$$\frac{da_N(v)^{-1}}{dv} \approx \frac{\Delta a_N(v)^{-1}}{\Delta v} = \frac{a_N(v_j)^{-1} - a_N(v_i)^{-1}}{v_j - v_i} \quad (3)$$

Assuming that $v_j - v_i$ is always a constant (this assumption is valid for almost all instrumental equipment), Eq. (3) can be written as

$$\frac{da_N(v)^{-1}}{dv} \Delta v \approx a_N(v_j)^{-1} - a_N(v_i)^{-1} = p \quad (4)$$

where p denotes an auxiliary function in order to simplify the notation. Since Eq. (4) defines positive and negative values, and these are decreased as a result of mathematical transformation, $|p|$ is calculated and the signals are amplified by the calculation of square root; but also, it is suggested to comeback to “more natural scale” $a_N^{-1} \rightarrow a_N$ and to search an adequate congruence with absorbance data by $1 + a_N$. By the above, Function P is defined to be

$$P = \frac{(1 + a_N)}{\sqrt{|p|}} \quad (5)$$

Finally, Eq. (5) can be normalized using the maximum value of P (p_{max}), thus

$$P_N = \frac{(1 + a_N)}{p_{max} \sqrt{|p|}} \quad (6)$$

Note that, equations have no limitations related to technique. Consequently, equations can be used to analyze spectra from other techniques such as Raman spectroscopy or ultraviolet-visible spectroscopy.

Material and methods

Reagents and equipment

Alcohols (Aldrich, St Louis, MO, USA) and carboxylic acids (Aldrich, St Louis, MO, USA) with different molecular weight were used as target samples. Alcohols were ethanol and *n*-butanol and *n*-hexanol, whereas carboxylic acids were formic acid, acetic acid and citric acid. Deionized water was used in all cases. These compounds were selected by practical importance of main functional groups associated with them: carboxylic acid (—COOH), carbonyl (—C=O) and hydroxyl (—OH). All reagents were analytical grade. Samples were analyzed by FTIR spectroscopy by attenuated total reflectance (ATR-FTIR) using an IRAffinity-1S spectrophotometer from Shimadzu Co (Kyoto, Japan).

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