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Mini Review

Functionally-enhanced derivative spectroscopy (FEDS): a powerful tool to increase of spectral resolution in the mid-infrared advanced analysis of complex samples–a mini review

Abstract

Functionally-Enhanced Derivative Spectroscopy (FEDS) is a simple, fast and easy to use deconvolution method based on the combination of derivative spectroscopy and simple functional algorithms. As analytical technique has demonstrated to be a powerful tool for analysis of spectral signals of mid-infrared spectra. In specific, FEDS produces the separation of overlapped signals through a transformation of the spectrum that consists of making the signals more acute and intense depending on the signal to noise ratio. The purpose of this review is to provide a theoretical and applied overview of ability of FEDS for the improving spectral analysis of complex samples with importance in materials, food and biomedical engineering, environmental sciences, microbiology, biotechnology and biological, chemical and physical science, among others.

Keywords: derivative spectroscopy, functional transformation, mid-infrared spectrum, deconvolution, signal overlap

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Manuel Palencia,[1] Viviana Garcés-Villegas,[1,2] Diego F Restrepo,[1] Jina M Martínez,[1,2] Luis R Anaya–Tatis,[2] Enrique M Combatt[3]

[1]Department of Chemistry, Universidad del Valle, Colombia
[2]Mindtech Research Group (Mindtech-RG), Colombia
[3]Department of Agricultural Engineering and Rural Development, Universidad de Cordoba, Colombia

Correspondence: Manuel Palencia, Department of Chemistry, Universidad del Valle, Campus Melendez, Building E-20, Street 100-00, Cali–Colombia,
Email manuel.palenci@correounivalle.edu.co

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Abbreviations: IR, infrared; FEDS, functionally-enhanced derivative spectroscopy; DFT, density functional theory; SNR, signal-noise ratio

Introduction

Background of analytical problem

Infrared spectroscopy (IR spectroscopy) is a well-known technique based on the interaction of IR radiation with the matter. By this interaction, changes of vibrational state of functional groups are produced.[1–5] These changes are visualized in the IR spectra as signals associated with the wavelength of vibration, or as usually is done in chemistry, with the wavenumber, but also, with the intensity of absorbed radiation (absorbance).[2,3] Thus, each molecule has associated a characteristic vibrational patter which gives qualitative and quantitative information about molecular structure. The component quantitative is resulting of Beer-Lambert Law which describes a linear relationship between the absorbance and the concentration.[2,3] However, as the number of components in the analytic sample increases, the vibrational patter is increased in complexity. The reason of the above is that each component into the sample has its own vibrational patter and, in consequence, overlap of signals is produced. In addition, the molecular vibration is affected by the chemical environment, or being the same, by the intra- and intermolecular interactions, and therefore, as a result of the above, the signal broadening is produced and overlap is increased. But also, fluctuations of signals, displacements and the presence of noise are factors which are usually identified in the typical IR spectra.[1–5]

Many applications of IR spectroscopy have been described, and these have been focused in the positive aspects of technique being generally omitted their limitations. Some applications for the study of complex and dynamic systems in microbiology and biotechnology are: to characterize molecular composition and stress response in foodborne pathogenic bacteria,[6] analysis of microbial cell,[7] identification and discrimination of bacteria,[8] real-time monitoring of nitrile biotransformations,[9] microbial biodegradation pathways,[10] monitoring of bacterial biofilm formation on implantable devices,[11] characterization of structural properties of fungal-bacterial biofilms.[12] Applications in other fields also have been described and these are easily localized in specialized publications.[1–5] From analytical overview, the quality analysis is directly related with the quality of information obtained. Thus, in a typical IR analysis, overlap and broadening of signals is not desired. However, in many cases this cannot be avoided and the analysis is strongly restricted. The above is a major problem when complexity of sample is increased (e.g., blood, biofilms, soils, animal and plant tissues, polymeric composites, among others), and therefore, the IR technique has seen limited their applications to relatively simple systems (e.g., individual molecules, binary systems) or to the identification of characteristic signals of one or more components in a mixture (e.g., identification of carbonyl groups of esters in a matrix of polypropylene).[6-11] In order to resolve these problems different strategies have been used, being the theoretical and computational approach, and the mathematical approach, the more generalized, including Fourier transform, Derivative spectroscopy and Functionally-Enhanced Derivative Spectroscopy (FEDS). The purpose of this review is to provide a theoretical and applied overview

about the ability of FEDS for the improving spectral analysis of complex samples with importance in materials, food and biomedical engineering, environmental sciences, microbiology, biotechnology, and biological, chemical and physical sciences, among others.

Previous approaches to FEDS

Theoretical and computational approach is based in theoretical modeling of vibrational patters of molecules by advanced procedures, as Density Functional Theory or DFT, thus, theorical spectrum of molecules is obtained by the combination of theory and calculations. However, its application requires specialized knowledge in quantum and computational chemistry, specialized software (e.g., Gaussian software), and a relatively high computational cost depending of complexity of target problem. But also, the use of this approach is limited to simple molecules and systems, where the predicted spectrum is depending of computational code used, in consequence, it not rare that theoretical spectrum differs of experimental spectrum. Many examples for the study of simple molecules have been published, by instance, vibrational analysis of nucleic acids,[13,14] amino acids as glycine and cysteine,[15,16] or biological components as N-Acetyl-D-glucosamine and D-Glucuronic Acid.[17] On the other hand, mathematical approach is based on to consider the spectrum as a continuous mathematical function and, therefore, several mathematical strategies can be used. The most common technique is the Fourier deconvolution or Fourier self-deconvolution algorithm.[18–21] However, though from a conceptual approach the Fourier self-deconvolution is simple, its application is limited by the complexity of computation, the appearing of negative intensities from calculations, the highly sensitive to the noise and the appearing of 'false' signals resulting of mathematical arguments without physical meaning.[18]

Other strategy is the derivative spectroscopy, mainly, the second-order derivate. The derivation process yields helpful features associated with the spectrum such as maximum and minimum points (first-order derivative) and points of inflection (second-order derivative). Thus, the first-order derivative is the slope of the "spectrum function" in function of wavenumber, or wavelength. Whereas the first-order derivative has a value of zero at the same wavelengths where the original spectrum has a maximum or minimum, the second-order derivative has a value equal to zero where the first-order derivative reaches a minimum or maximum absorbance; but also, these points correspond to points of inflection in the original spectrum. In this way, the first and second order derivatives facilitate the extracting of features specifically associated with the spectra; however, upper derivatives are hardly rationalized since these don't show a direct relation with original function.[22,23] In addition, the most important effect of the derivative method is that broad bands are suppressed in comparison with sharp bands and, in consequence, this suppression increases with the increase of derivative order.[22–27] An unwished effect of the derivative spectroscopy is that the signal-noise ratio (SNR) decreases as derivatives with higher orders are used; therefore, for the derivative process, it is important the control of the degree of smoothing that is applied in order to adapt the procedure to different analytical problems.[22,23]

FEDS spectroscopy: fundaments

In contrast with the strategies previously described, FEDS is a simple method for the deconvolution and the increase of spectral resolution of signals, based on the transformation of spectrum by the use of derivative algorithm enhanced by functional transformations. In addition, it has the following advantages: easy use, no require high computational capacity, adaptability according to objective, no requires advanced software, and produces the deconvolution of spectrum coherently with original IR spectrum.[28] FEDS algorithm is based on the application of functional transformations of spectrum and first-order differentiation. By FEDS, the spectrum is considered a collection of data which correspond to points of function where for each value of wavenumber (v) is obtained one absorbance value (a). In consequence, a is function of v, and therefore it can be written to be **w**, where **w** denotes a function **w:(*v*)** which describes the IR spectrum. After, it is defined a new function **y** which is obtained by the calculation of inverse of respective absorbance. Thus, if a is the absorbance of **w(v)** then a^{-1} will be the absorbance of **y(v)**. Later, first-order derivate of **y(v)** is calculated with a 'small' consideration.

Since the difference between two adjacent values of v is constant, the function **w** is given by the difference between absorbances instead of quotient between the difference of absorbance (i.e., $a_{j+1} - a_j$ where j denotes the j-th position in the spectrum) and the difference between respective v (i.e., $v_{j+1} - v_j$). The above defines the auxiliary function p (the notation p comes from the Spanish word '*primera*' alluding to the use of the first derivative). The following step consists in to use the mathematical operator $1/(|x|)^{0.5}$ where x denotes any mathematical argument, and it is used to define the working function called Function P. Note that this operator is equal to scale factor defined under the wavelet concept, which is used to define the general expression of 'mother wavelet'. Function P is defined for each v_j as

$$P_j = \frac{1 + a_j}{\sqrt{|p_j|}} \tag{1}$$

where $(1 + a_j)$ is an amplification factor for the assignation of a weight congruent with absorbance intensity (i.e., small values of absorbance in the experimental spectrum will be amplified using small values of a_j since $1+ a_j$ will be a small factor, contrary to the expected for large values of a_j). It is important avoid confusions with the notation used, and therefore it is suggested the use of the same terms in order to achieve a language uniformity. Details description is given by Palencia.[28]

An important aspect for the correct application of FEDS is the pre-treatment of data. For each region of spectrum being analyzed, data must be auto-scaled with respect to the values of minimum and maximum absorbances (a_{min} and a_{max}, respectively).

$$b_j = \frac{a_j - a_{min}}{a_{max} - a_{min}} \tag{2}$$

where a_j and b_j are the experimental absorbance and the corresponding auto-scaled absorbance, respectively. In order to avoid calculation mistakes resulting to scaling from 0 to 1 during the application of FEDS algorithm, the zero absorbance was approximated by the calculation of average value between two adjacent values of absorbance satisfying that $b_{j-1} < b_j < b_{j+1}$ with $b_j = 0$ (deterministic approximation). Since derivative spectrum is strongly sensitive to the noise in the original signal, the smoothing of spectral noise must be decreased by the use of average-based spectral filter (ABSF).[28] ABSF is given by

$$ABSF(b_i; N = 20) = \frac{1}{3}\sum_{j}^{j+2}\left(b_j\right)\Bigg|_{N=1}^{N=20} \tag{3}$$

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ABSF is the moving average with a data window of 3 and 20 cycles ($N = 20$). Thus, for each b_j, b_{j+1} and b_{j+2} the corresponding average value is calculated, and subsequently, this procedure is repeated N times. However, as the spectrum line function in the absorbance domain is modified by the use of Equation 3, the same transformation of data is performed on values of wavenumber (v) in order to correct the displacements respect to original spectrum (*i.e.,* maximum points in original spectrum should be the same in the original and smoothed spectra).[28]

FEDS applications

FEDS has been used for the structural study of humin and its interaction with humic acids by Fourier-transform mid-infrared spectroscopy permitting to identify the wavenumbers of hydroxyl groups of humic acids in extracted of humified organic matter.[29] In a similar context, during edaphology studies, FEDS has been used for the study, by attenuated total reflectance spectroscopy, structural changes of humified organic matter by chemical perturbations via alkaline dissolution. Results showed that FEDS can be used to increase the differentiation between soil spectra, and possibility the identification of signals highly overlapped.[30] In addition, FEDS have been used to determine weak signals in spectra of nitrogen-fixing bacterial biofilms.[31] On the other hand, FEDS was used to explore the deconvolution of surface plasmon of inorganic nanoparticles. Though contraction of signal was obtained, results permits conclude that FEDS technique can be used for the building of mixture models of spectral signals in order to achieve a correlation with their components.[32] The mid-infrared spectral characterization of fish scales: "Bocachico" (*Prochilodus magdalenae*) was performed by FEDS permitting the characterization of collagen and identification of hydroxyapatite.[33] In the study of binary mixture, FEDS was used for the solve the problem of the overlap of spectral signals in mixtures of triethylamine-acetone demonstrating its capability to extract signals from small fluctuations of line function of IR spectra.[34]

Conclusion

FEDS is an analytical tool which enormous potential in the analysis of complex systems. It has as advantage its easy implementation and interpretation. In addition, it is adaptable to much types of problems and maximize the potential use of IR spectroscopy. Though the most of researches has been centered to the use of IR spectra, it is concluded from review of fundaments that FEDS can be implemented in any functional relationship of physical variables. On the other hand, FEDS transform of IR spectra permits the building of new and more specific spectral libraries, of target substances in many multicomponent systems with importance in biotechnology and bioengineering. In addition, it eases the comparison of spectra and the study of spectral signals with very low intensities permitting to extract analytical information from signal-noise mixtures, and the deconvolution of overlapped signals.

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Conflicts of interest

Authors declare that there is no conflict of interest.

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