FILTERING AND DIFFERENTIAL PROPERTIES OF WAVELET TRANSFORM AND ITS APPLICATION IN ANALYTICAL CHEMISTRY *

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Abstract. The theory shows that the continuous wavelet transform can be decomposed in two operations: a convolution with a particular filter impulse response followed by a derivative. This filtering properties, which are not related to the well known filters used in the discrete transform, are investigated for some common wavelet families.

Than all these properties are applied to the problem of determination of the components in overlapping gaussian functions affected by noise. An application to sample analysis in overlapping multicomponent chromatogram has been presented.

1. Introduction. Theory shows that wavelet transform could be seen as a filtering operator combined with a derivative [6]. According to this property, some of the most common wavelets can be classified. This can be successfully applied to the problem of determination of the components in overlapping gaussian signals affected by noise.

The wavelet transform is briefly introduced in Section 2 with particular attention on its differential properties. This section is also dealing with the classification from this point of view and shows that the considered wavelet functions (of order 1 and 2) are associated to band-pass and low-pass filter responses. In section 3 it is presented the following problem: given a signal, known to be the sum of n independent gaussians, determine the number of components and their centres. It is shown that this problem is well posed but can be ill conditioned. For practical applications of this problem, see [11], [7] and [3]. Then a method to approach the proposed problem is described. Using this method, in Section 4 we discuss the sample analysis in overlapping multicomponent chromatogram and give some examples of experimental data.

2. Wavelets and filtering properties. In this work the following definitions are adopted: a wavelet of order $m > 0$ is a function $\psi \in L^2(R)$ such that:

1. $\psi^{(l)}(x) \in L^2(R) \quad \forall l = 0, \ldots, m-1$
2. $\psi^{(l)}(x) \overset{|x|\to\infty}{\longrightarrow} 0 \quad \forall l = 0, \ldots, m-1$
3. $\int_{-\infty}^{+\infty} x^l \psi(x)dx = 0 \quad \forall l = 0, \ldots, m-1$

The integral $\int_{-\infty}^{+\infty} x^l \psi(x)dx$ is called the l-th moment of ψ, so property (3) requires that a wavelet of order m has exactly m vanishing moments.

Let $\psi_s(x) = \frac{1}{s}\psi(\frac{x}{s})$ be the dilation of $\psi(x)$ by the scale factor s. The wavelet transform of a function $f(x) \in L^2(R)$ is defined by

$$Wf(s,x) = f * \psi_s(x) \tag{2.1}$$

where $*$ represents the convolution operator

$$(f * g)(x) = \int_{-\infty}^{+\infty} f(t)g(x-t)dt$$

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Now we are going to put in evidence that the wavelet transform of a function f could be seen as a differential operator applied on f after filtering with a linear time invariant filter. Let $\theta(x) \in C^1(R)$ be the impulse response of a filter and $\theta_s(x) = \frac{1}{s}\theta(\frac{x}{s})$. Calling

$$\psi(x) = \frac{d\theta(x)}{dx}, \tag{2.2}$$

the wavelet transform defined with respect to ψ is given by

$$Wf(s,x) = f * (s\frac{d\theta_s}{dx})(x) = s\frac{d}{dx}(f * \theta_s)(x) \tag{2.3}$$

which is proportional to the first derivative of f after filtering with θ_s.
Analogously, if $\theta(x) \in C^2(R)$ and

$$\psi(x) = \frac{d^2\theta(x)}{dx^2}, \tag{2.4}$$

then the transform (2.3) becomes:

$$Wf(s,x) = f * (s^2\frac{d^2\theta_s}{dx^2})(x) = s^2\frac{d^2}{dx^2}(f * \theta_s)(x) \tag{2.5}$$

which is proportional to the second derivative of f after filtering with θ, and so on by increasing the order of the derivative.
We recall here the following proposition:
Proposition 1.
A wavelet ψ with a fast decay has n vanishing moments if and only if there exists a function θ with a fast decay such that

$$\psi(x) = (-1)^n\frac{d^n\theta(x)}{dx^n}$$

For the proof see [5, p. 169].
As a consequence, any wavelet function of any order can be expressed as the derivative of a function $\theta(x)$. Remembering that θ could be seen as the impulse response of a filter, it is interesting to study the behaviour of such a filter for some of the wavelets we are going to use in this work.

Now three different families of wavelets are analyzed: spline wavelets, gaussian wavelets and Symmlets. Their filtering properties, described in the previous section, are evaluated studying the function $\theta(x)$, which is the impulse response of the filter associated to each wavelet.

Equation (2.3) shows that the parameter s of the wavelet transform $Wf(s,x)$ determines a particular scaling for the filter response θ, because the function f is convolved with θ_s, the dilation of the function θ. It follows that the parameter s does not affect the character of the filter, but only rescales the frequency axis and consequently the cutoff frequency. So we can limit our study to the case $s = 1$.

Recalling (2.2), $\theta(x)$ can be obtained by integrating the wavelet function $\psi(x)$; the frequency response of the filter can be exploited applying the Fourier transform on the impulse $\theta(x)$.

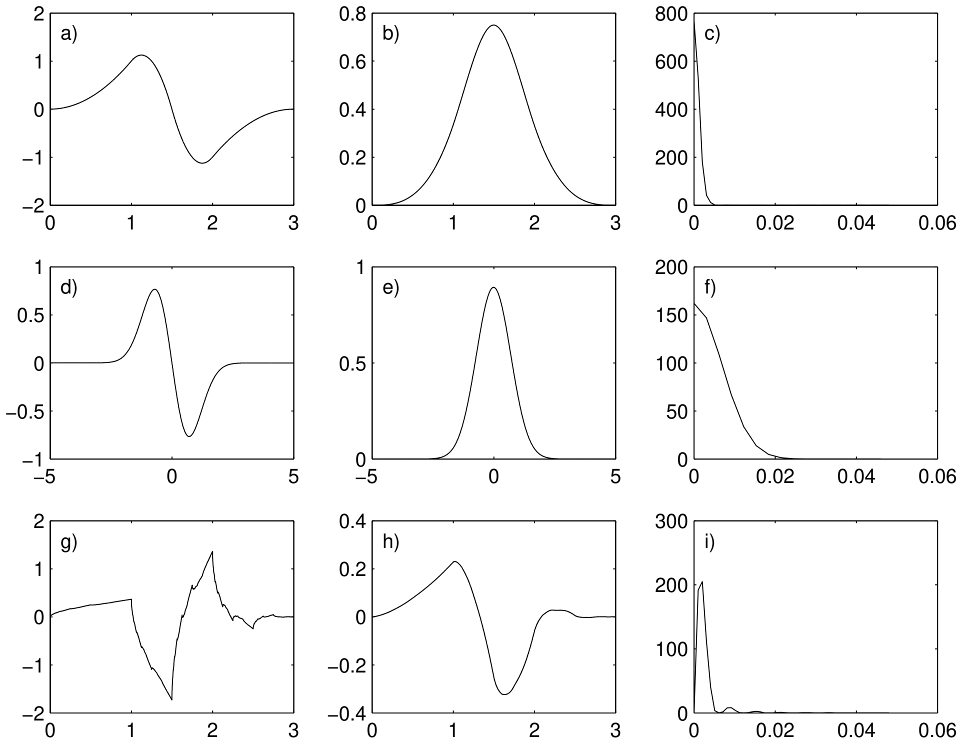

FIG. 2.1. *First column: graphs of a) quadratic spline wavelet, d) first order gaussian wavelet, g) second order Symmlet. Second column: integral functions of the respective wavelets. Third column: Fourier transform of integral functions which represents the frequency response before derivation.*

These results are presented in Fig. 2.1. It can be observed that the θ functions of the quadratic spline and gaussian wavelets lead to low-pass frequency responses with different steepness. Conversely Symmlet wavelet is associated to a band-pass response.

Analogously, if the order of a wavelet ψ is $m \geq 2$, it is possible to find a function $\theta(x)$ that satisfies (2.4). As seen in (2.5), the wavelet transform of a function $f \in L^2(R)$ is proportional to the second derivative of f after filtering with θ. So, starting from a given wavelet ψ, we can calculate θ by integrating twice the function ψ. Finally, the frequency response of the filter θ is obtained applying the Fourier transform on θ.

These results are represented in Fig. 2.2. Here we can see that only the maxican hat wavelet has preserved the low-pass characteristic, while the others have a band-pass response.

For a given application, the filtering characteristics (low-pass, high-pass, etc...) can be a criterion for the choice of a wavelet.

3. Statement of the problem and description of the method. Let us consider the following problem: given a function f, known to be the sum of n independent gaussians,

$$f(x) = \sum_{i=1}^{n} \alpha_i e^{-\frac{(x-c_i)^2}{\sigma_i^2}}, \tag{3.1}$$

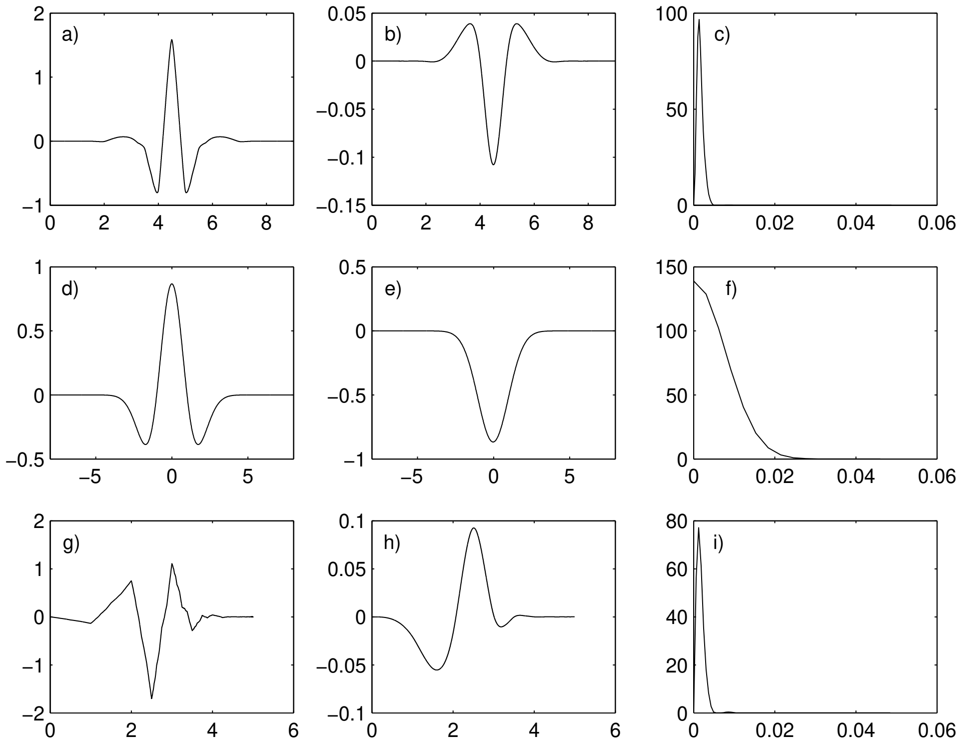

FIG. 2.2. *First column: graphs of a) cubic spline wavelet, d) mexican hat wavelet, g) third order Symmlet. Second column: graphs obtained integrating twice the wavelet functions. Third column: Fourier transform of integral functions which depicts the frequency response before derivation.*

$$c_i \neq c_j \quad i \neq j$$

determine the value of $n \in N^+$ and the n triplets $(\alpha_i, c_i, \sigma_i)$.

It can be shown that this is a well posed problem because gaussians with different centres are linearly independent. Unfortunately, it can be very ill conditioned, especially when two among the centres are close each others. Consider this example: let f_1^ϵ and f_2^ϵ be functions of the type 3.1, with $n = 2$, such that

$$f_1^\epsilon = \alpha_1^1 e^{-\frac{(x-c_1)^2}{\sigma^2}} + \alpha_2^1 e^{-\frac{(x-c_2)^2}{\sigma^2}}$$

$$f_2^\epsilon = \alpha_1^2 e^{-\frac{(x-c_1)^2}{\sigma^2}} + \alpha_2^2 e^{-\frac{(x-c_2)^2}{\sigma^2}}$$

$$c_2 = c_1 + \epsilon, \quad \alpha_1^1 = \alpha_2^2 = 101, \quad \alpha_2^1 = \alpha_1^2 = 1$$

The continuity of these functions with respect to the parameters yields

$$\lim_{\epsilon \to 0} \| f_2^\epsilon - f_1^\epsilon \| = 0 \tag{3.2}$$

Remembering that given a function f_1^ϵ our goal is to determine its parameters $c_i, \alpha_i, \sigma_i \quad i = 1, 2$, the conditioning of the problem is a measure of how the parameters change when

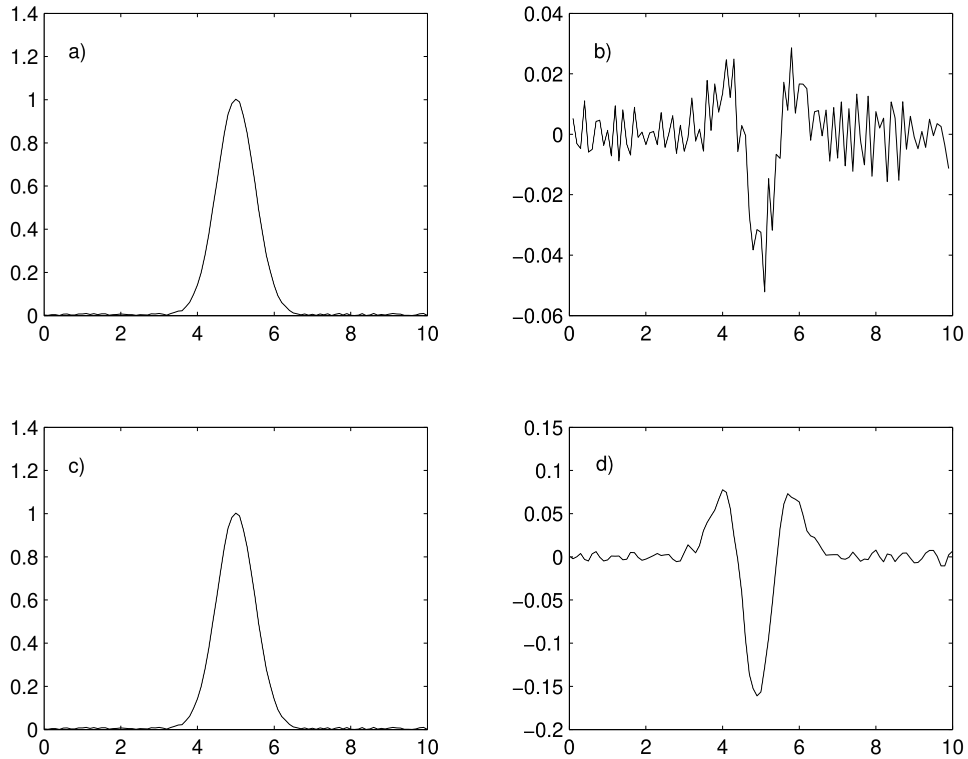

FIG. 3.1. *a) and c) Gaussian function affected by -40dB noise, b) second derivative of a), d) two times wavelet transform of c) with quadratic spline wavelet*

f_1^ϵ is perturbed. So an estimation of the conditioning on the parameters α is

$$\frac{\alpha_1^1 - \alpha_1^2}{\|f_2^\epsilon - f_1^\epsilon\|}$$

It can be observed that $\alpha_1^1 - \alpha_1^2 = 100$ so

$$\lim_{\epsilon \to 0} \frac{\alpha_1^1 - \alpha_1^2}{\|f_2^\epsilon - f_1^\epsilon\|} = +\infty$$

It means that acting on ϵ the conditioning can be increased arbitrarily.

This explains why many authors ([7], [9], [10]) are taking the following *resolution* index:

$$R = \max_j \frac{c_{j+1} - c_j}{K(\sigma_{j+1} - \sigma_j)}$$

as an estimation of the conditioning of the problem, where $K = 2\sqrt{2ln2}$. The number R represents the degree of overlap of two adjacent peaks, so small values of this index correspond to a worse conditioning of the problem, and vice versa.

This is the complete formulation of the problem. However, in many practical applications, n and gaussian centres c_i are the most important parameters, so we can

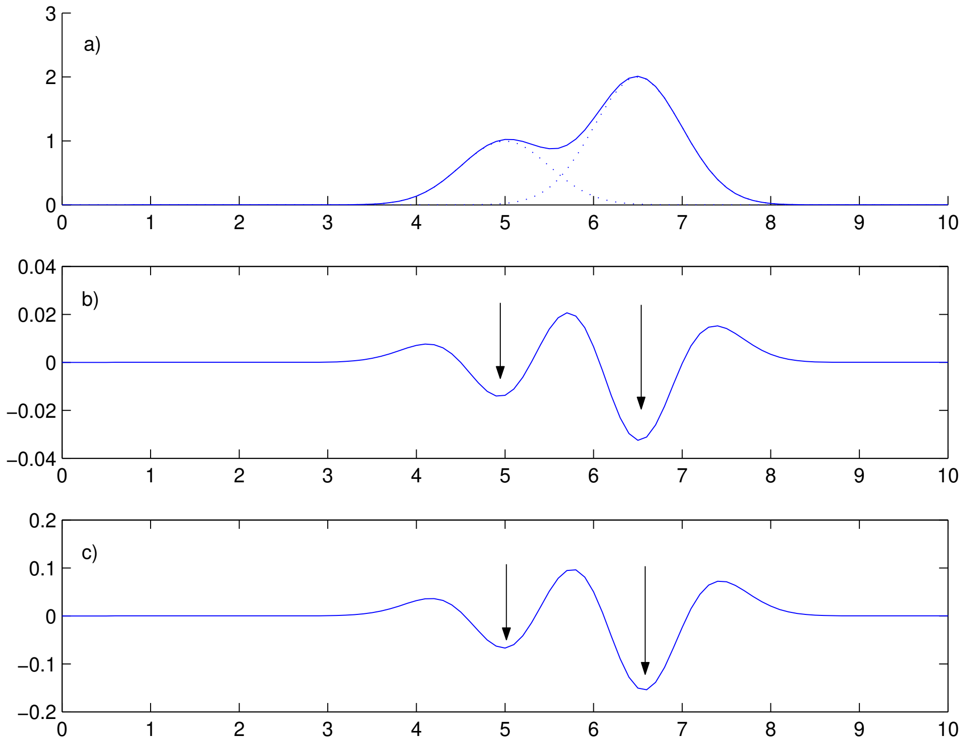

FIG. 3.2. *a) Well conditioned case: sum of two gaussian functions (single components dotted) with resolution index R=0.64, b) two times wavelet transform of a) with quadratic spline wavelet, c) wavelet transform of a) with mexican hat wavelet*

restrict this work to a simplified formulation, where only those parameters have to be determined. Some example of these applications can be found in [11], [7] and [3]. The work [7] discusses the sample analysis in overlapping multicomponent chromatogram, a problem where the main information is the centres of the gaussian components of the signal; also the paper [3] is about separation of overlapped peaks of capillary electrophoresis (a highly effective liquid separation technique) signals for amino acid mixed solutions and inorganic ion solutions. For this kind of applications, typical values of the resolution R ranges from 0.2 to 1.5. Note that (3.1) is only a theoretical model of the problem. Actually experimental data are affected by noise and the components could not be gaussian functions but only curves with similar shape; this is very important, especially when the problem is ill-conditioned.

If f is a gaussian function, its second derivative has a minimum exactly in the centre of f. More in general the derivative of order $4n-2 \quad n = 1, 2, \dots$ has a minimum in the centre and the derivative of order $4n \quad n = 1, 2, \dots$ has a maximum in the centre. Consider the sum of n gaussians; if it is not an ill conditioned case, that is the centres are not too close each others, it can be observed that there exists an integer m such that $f^{(2m)}$ has n critical points. Furthermore these points are near the centres of each component. Unfortunately simple deriving the signal does not lead to useful results, due to the noise amplified by the derivative operation, as can be seen in Fig. 3.1a and 3.1b. To face this problem it could be useful to filter the noise

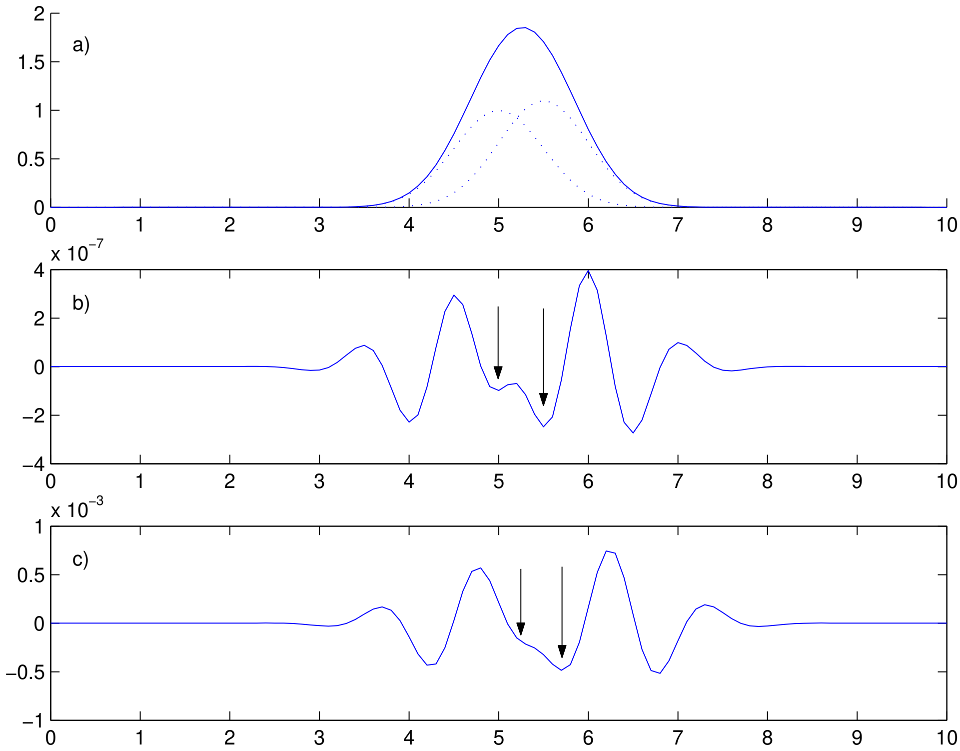

FIG. 3.3. *a) Ill conditioned case: sum of two gaussian functions (single components dotted) with resolution index R=0.21, b) ten times wavelet transform of a) with quadratic spline wavelet, c) five times wavelet transform of a) with mexican hat wavelet*

out of the signal, in the frequency ranges where gaussians have very low energy. This suggest to use wavelet transform because it filters the signal and then calculates the derivative. Because gaussian functions have energy located in the lower frequencies, wavelets associated with low-pass responses have to be choosen. Two of the wavelets which satisfies these requirements are the quadratic spline wavelet and the mexican hat wavelet

This single operation performs a derivative on the signal after filtering out the high frequencies where gaussians have low energy, as shown in Fig. 3.1c and 3.1d. Recall that the quadratic spline wavelets are of order 1 and that mexican hat wavelets are of order 2, so they respectively perform a first order and second order filtered derivative. If we are interested in a derivative of order $2n$, using a wavelet of order k, we have to repeat the transformation $\frac{2n}{k}$ times. This means that at each repetition the transformation is applied on the result of the previous repetition. After the transformation we could have many critical points, especially if we repeat the transformation many times (like in Fig.3.3b); in this case the centres should be searched in the critical points near the maximum of the original signal, where all the components are concentrated.

To illustrate the process of component detection, consider the sum of two gaussians, the first with centre $c_1 = 5$, $\sigma_1 = 0.5$ and amplitude $\alpha_1 = 1$, the second with centre $c_2 = 6.5$, $\sigma_2 = 0.5$ and amplitude $\alpha_2 = 2$, as shown in Fig. 3.2a. The resolution R for this problem is 0.64. We can transform this signal twice using the quadratic

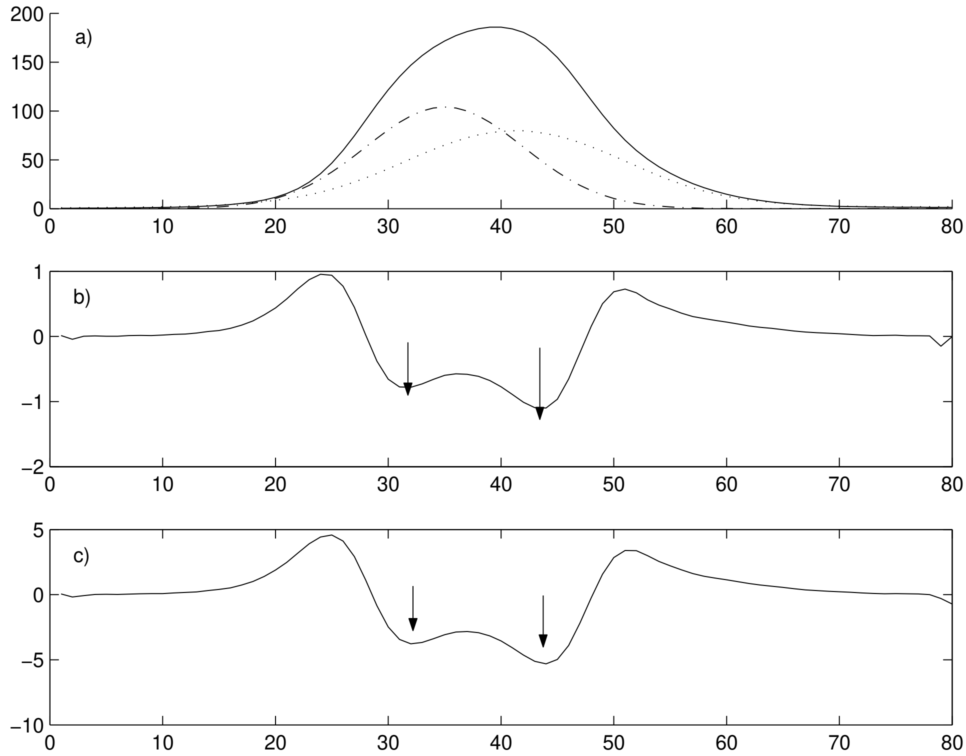

FIG. 4.1. *a) Chromatogram of the mixture of lead (Pb) and thallium (Tl), both with concentration of 0.3μg/l (Tl dotted graph, Pb dash-dot graph). b) twice wavelet transform of a) with quadratic spline wavelet, c) wavelet transform of a) with mexican hat wavelet*

spline wavelet (Fig. 3.2b) or once with the mexican hat wavelet (Fig. 3.2c), obtaining in both cases a filtered second derivative. It can be observed that the number of minima of the transformed signals is the same of the number of the components of the original signal. Besides, the minimum points are good approximations of the centres of the two gaussian components, that's because the resolution index is quite good.

As an example of a bad conditioned case, consider the sum of two gaussians, the first with centre $c_1 = 5$, $\sigma_1 = 0.5$ and amplitude $\alpha_1 = 1$, the second with centre $c_2 = 5.5$, $\sigma_2 = 0.5$ and amplitude $\alpha_2 = 1.1$, as shown in Fig. 3.3a. For this problem (resolution $R = 0.21$), it has been necessary to calculate the derivative up to order 10, to display the minimum points, and so an estimation of the centres positions.

4. Experimental section. In this section the method described above is applied on experimental data coming from chromatograms. Chromatography is a process widely used in analytical chemistry for the separation of compounds in sample mixtures. In a chromatogram, each compound of a mixture generates a gaussian waveform; the position of the center of each gaussian identifies the componente chimica. Different compounds can overlap and generate a signal which is a linear combination of gaussians. Given this signal, the problem is to find out the number of components and their centres to detect the compounds of the mixture. For this kind of application, a relative error of 10% is acceptable.

We propose now the chromatograms of two test mixtures of lead (Pb) and thallium

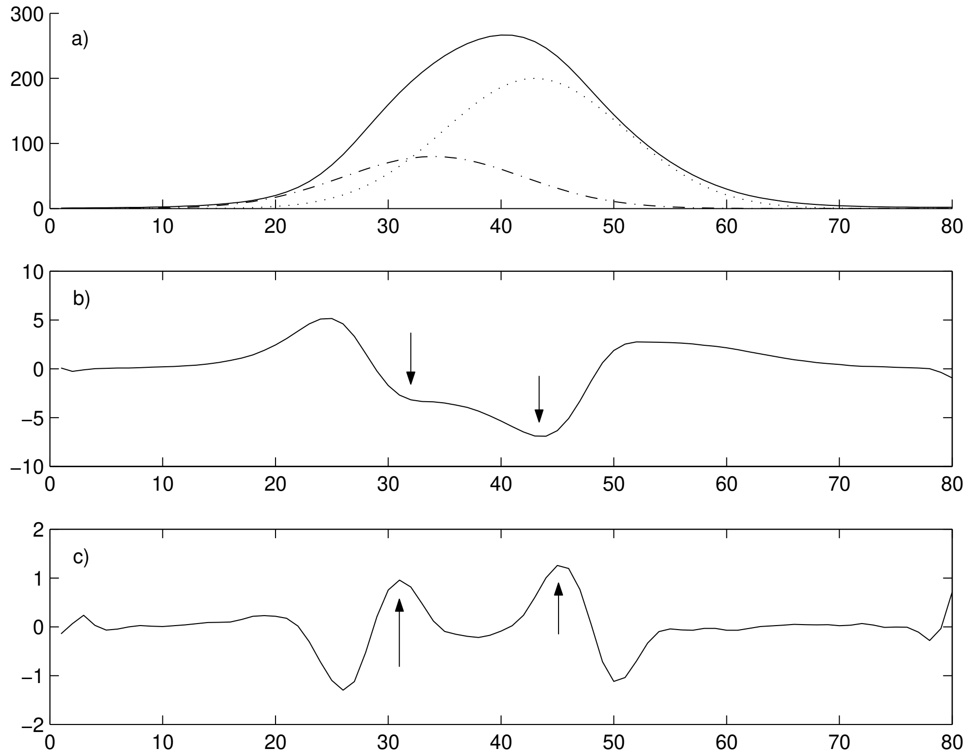

FIG. 4.2. *a) Chromatogram of the mixture of lead (Pb) and thallium (Tl), with concentration of 0.2μg/l and 0.7μg/l respectively (Tl dotted graph, Pb dash-dot graph). b) wavelet transform of a) with mexican hat wavelet, c) two times wavelet transform of a) with mexican hat wavelet*

(Tl) with different concentrations, as shown in Fig. 4.1a and 4.2a (the dotted graphs are the signals of the pure(?) elements). The signal 4.1a has been transformed twice with the quadratic spline wavelet (Fig. 4.1b) and once with the mexican hat wavelet (Fig. 4.1c).

It can be observed that both the transformed signals have two minimum points which denotes the number of component of the mixture. These minimum points are located near 32 (Pb) and 44 (Tl) which approximate the centres of the signals of the pure(?) elements. The correct known values are 35 for the lead and 41 for the thallium, so the relative error is inside the acceptable range.

The signal in Fig. 4.2a is not conditioned as good as the signal in 4.1a: in fact its second derivative (Fig. 4.2b) has not the two minima corresponding to the two components of the signal; fourth order derivative is needed to exploit them (Fig. 4.2c). In this case, as said on the beginning of section 5, the centres of the components have to be searched on the maximum points of the transformed signal. Again, they are located near 32 (Pb) and 45 (Tl) and this result is correct because this chromatogram is referred to the same elements of the previous case.

5. Conclusions. In this paper it has been shown that the wavelet transform could be seen as a filtering operator combined with a derivative. Some of the most common wavelets have been classified according to these properties.

In the second part of this work, these properties have been applied to the problem of determination of the components in overlapping gaussian functions affected by noise. The proposed method allows to determine with good approximation the number of the components and their centres even in a not well conditioned cases.

Acknowledgment. The authors are very grateful to Prof. Luigia Puccio, Universitá di Messina, Dipartimento di Matematica, for her helpful suggestions, and Dr. Marina Cocchi, Prof. Renato Seeber and Dr. Alessandro Ulrici, Dipartimento di Chimica, Universitá di Modena e Reggio Emilia, Italy, for their suggestions and for providing the experimental data.

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