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Critical Analysis of Spectral Deconvolution Methods

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Abstract: Spectral deconvolution methods are critically reviewed using simple mathematical description and graphical illustration. It is shown that all methods are based on the compromise between the maximum resolution enhancement and the minimum intensity of the side lobes. It is emphasized that there exists no general solution ("panacea") for all deconvolution problems and the optimal deconvolution algorithm should be chosen with regard to the particular analytical problem under study. The general approach to selecting the quasi optimal algorithm is suggested.

Keywords: Spectral deconvolution; Tikhonov regularization; self-deconvolution; artificial improvement of the spectral resolution; inverse filtering.

I. Introduction

Spectrometry is one of the most widespread theoretical and experimental physical methods, which has been employed in various fields of science and technology for more than a century [1]. Computer-enhanced industrial and laboratory spectral instruments are powerful tools used by researchers and practitioners in physics, chemistry, biology and medicine, pharmacology, metallurgy, food industry, astronomy, archaeology, criminalistics, as well as in the environment control. Using smart mathematical software algorithms, it is possible to automatically obtain correct information about the samples under study. In general, spectral data processing can be divided into two sequential steps: pre-processing of raw data and extracting the necessary information [2]. The main goal of the first stage is reducing the noise, removing the non-zero baseline and resolving overlapped spectral components (lines and bands). Overlapping of spectral components is accounted for their broadening due to the instrumental distortions (e.g., limited maximum delay time in the interferogram obtained using Fourier-transform infrared spectrometers and non-zero width of the instrumental function of monochromators) and inter- and/or intra-atomic and molecular interactions (e.g., Stark broadening in dense plasma [3], spin-spin interactions in NMR-spectroscopy [4], inter- and intra-molecular associations in IR-spectroscopy of liquids [5]) in the samples under study. Overlapping spectral components can be only partly separated by spectral data processing usually referred to as deconvolution. The artificial resolution improvement (spectral peak sharpening) and decomposition of a composite spectrum into individual pure-component spectra are sometimes viewed as a deconvolution process in a more general sense. From the theoretical point of view, deconvolution is generally considered as an *inverse problem*, which is commonly encountered in practical applications [6].

Since the 1930s, deconvolution has been the subject of numerous studies in optics, spectroscopy, analytical chemistry, and chemometrics [7-21]. *Derivative spectroscopy* (DS), which is one of the first deconvolution methods, is now widely used for pre-processing [11, 12]. Since, in this method, the low-order polynomial background is suppressed and spectral resolution is enhanced, the first- and second-order spectrum derivatives are commonly used for qualitative and quantitative analysis in many practical applications. Another method widely used in spectroscopic practice is *Fourier self-deconvolution* (FSD) [7-10, 13, 14], which was developed on the basis of Fourier transform spectroscopy [9]. The mature period of deconvolution started with the approach of viewing deconvolution as part of *Digital Signal Processing* (DSP) of spectral data in the framework of the functional engineering model of a spectral instrument (see review [15]). A set of effective deconvolution algorithms based on a complex of mathematical tools, such as *digital filters*, *spline approximation*, and *Tikhonov regularization* (*Ridge regression*), is described in [15-21]. General mathematical theory of deconvolution has its foundation in the integral equation theory [23].

Unfortunately, the researchers who are engaged in the deconvolution problem often present similar results using different terminology and mathematical tools. For example, in NMR spectroscopy, mathematical correction of instrumental imperfections is referred to as *reference deconvolution* (see references in [24]). Moreover, the use of formal mathematical approach makes it difficult for the reader who was brought up on classical concepts of optics and spectroscopy [7-10, 25] and is unfamiliar with DSP to gain detailed understanding of deconvolution and viewing the problem as a whole.

In the present spectroscopy-oriented analytical review, the most common methods of deconvolution of overlapping symmetrical spectral components are critically discussed. The advantages and disadvantages of these methods are demonstrated using sufficiently simple mathematical tools which should be clear to wide audience.

In what follows, for the sake of simplicity, term "line" is used for short of phrase "line and band". Standard algebraic notations are used throughout the article. All calculations were performed and the plots were built using the MATLAB program.

II. Theory

Before discussing the deconvolution problem, let us give some important definitions:

1. *Measured spectrum* (F_{ms}) is the spectrum obtained using a spectral instrument (SI) under certain internal (determined by the instrumental parameters) and external (e.g., temperature, pressure) conditions of the measurement. Changes of these parameters introduce random (noise) and systematic (e.g., drift) errors into F_{ms} .
2. *Instrumentally undisturbed spectrum* (the "true" spectrum, F_{tr}) is the spectrum obtained using an ideal SI, which does not disturb spectral lines. The positions and the line form parameters depend only on those external and internal factors which affect the physicochemical properties of the sample under study. Changes of the sample state give rise to random and systematic errors of F_{tr} . Employing special sample stabilization techniques may substantially decrease these errors. However, some systematic errors are, in principle, instrumentally irremovable (e.g., wavelength-dependent light scattering) and can only be corrected mathematically.
3. *True sample spectrum* (F_{ts}) is an instrumentally undisturbed spectrum obtained for the given physicochemical parameters of the sample. Spectroscopists have always dreamed of precise theoretical evaluation of F_{ts} [22].
4. *Quasi ideal spectrum* (F_{qid}) for a particular problem to be solved has the resolution that allows obtaining information (with the accuracy meeting the problem requirements) on the necessary parameters of the spectral lines. F_{qid} may be baseline-free and contains random noise at acceptable level. The baseline and the noise can be essentially decreased in the preprocessing phase of spectrum treatment.
5. *Deconvolution* is transformation of the measured spectrum (F_{ms}) into the one which is as close to F_{tr} as possible.
6. *Artificial improvement of spectral resolution (pseudo deconvolution, PS)* is transformation of the measured spectrum into the one which is as close to F_{qid} as possible. PS is performed using mathematical methods of deconvolution and other transformations of measured spectra (e.g., derivative spectroscopy [11, 12]). In some cases, the PS procedure (e. g., spectrum differentiation) leads to significant disturbances of the F_{ms} form. Terminological confusion between deconvolution and PS is quite common in literature. The reasons for such confusion and the physical foundations of PS are discussed below.

2.1 Deconvolution

It is well known that, for any real SI, the main factor defining the differences between the measured and the true spectrum is the non-zero width of monochromatic radiation [25]. Therefore, the measured spectrum can be represented as a convolution of the true spectrum with the instrumental function of the SI (or impulse response function in DSP), $K(x - x')$:

$$F_{ms}(x) = \int_{-\infty}^{\infty} K(x - x') F_{tr}(x') dx', \quad (1)$$

where x is the abscissa of the spectrum (*the spatial domain*) (e. g., wavelength). This equation is referred to as a *forward model of a spectrometric transducer* (SI in our notions) [15] or, in mathematics, as the *Fredholm first-kind integral equation*, where K is the *kernel* [23]. It was shown [26] that the smoothing properties of the kernel causes information loss in the convolution process (Eq.1). This loss can be only partly compensated in the deconvolution process by using *a priori* information on F_{tr} . The common assumption of K being independent on x' (the case of *stationary convolution*) is valid only for relatively narrow spectral intervals. For example, this assumption is violated by changing the slit width in different spectral ranges. Therefore, a simple generalization of Eq.1 is *non-stationary convolution* [27]:

$$F_{ms}(x) = \int_{-\infty}^{\infty} K(x - x', x') F_{tr}(x') dx'. \quad (2)$$

Another form of Eq. 1,

$$F_{ms}(x) = \int_{-\infty}^{\infty} K(x - x', x) F_{tr}(x') dx', \quad (3)$$

is referred to as *non-stationary combination* [27]. The second variable in the kernel differs in Eqs. 2 and 3. In contrast to Eq.1, Eqs. 2 and 3 cannot be considered as superpositions of impulse responses [27].

Precise expression for instrumental function can be experimentally obtained only for stationary deconvolution in some rare cases (e.g., [28]). Numerous mathematical models of instrumental functions, evaluated theoretically by analyzing distortions in optical and electronic parts of the SI, are reviewed in [25]. Generally speaking, deconvolution is the solution of an inverse ill-posed problem (Eqs. 1 and 2), where minor disturbances of the instrumental function and of the measured spectrum (e.g., noise) may cause uncontrolled computational errors of $F_{tr}(x)$. Common mathematical methods, which allow obtaining a stable solution, are usually based on *priori*

assumptions concerning the mathematical representation of the instrumental function and/or its properties. To avoid uncertainties in instrumental function modeling, various robust algorithms of solving Eqs. 1 and 2 either by forward or by inverse modeling have been developed [15].

A. Tikhonov-regularized deconvolution in the spatial domain for known kernel.

Using numerical integration regularized by Tikhonov method [29], Eq. 1 can be approximated by the following matrix equation [30]:

$$(\mathbf{K}^T \mathbf{K} + \alpha \mathbf{I}) \mathbf{F}_{tr} = \mathbf{K}^T \mathbf{F}_{ms}, \quad (4)$$

where $\mathbf{K}$ is the kernel matrix, T is the transpose symbol, α is the regularization parameter, and $\mathbf{I}$ is the identity matrix. Each row of matrix $\mathbf{K}$ includes the discretized kernel function, which is successively shifted from the low to the high integration limit in Eq. 1.

The need for regularization arises from the fact that matrix $\mathbf{K}^T \mathbf{K}$ is ill-conditioned (condition number is too large), which results in great sensitivity of the solution of Eq. 4 to small perturbations of $\mathbf{F}_{ms}$. The true spectrum is estimated by

$$\hat{\mathbf{F}}_{tr} = (\mathbf{K}^T \mathbf{K} + \alpha \mathbf{I})^{-1} \mathbf{K}^T \mathbf{F}_{ms}. \quad (5)$$

Some well-known algorithms of finding the solution of Eq. 4, based on non-negative constrain ($\hat{\mathbf{F}}_{tr} \geq 0$), are described in [16, 31]. The drawback of approximation (4) is evaluating of the integral with infinite limits (Eq.1) using a finite number of linear equations.

B. Deconvolution in the frequency domain for known kernel.

Stationary convolution (1) from the spatial (x) to the frequency (ω) domain is commonly implemented using integral Fourier transform (FT) [9]:

$$\tilde{F}_{ms}(\omega) = \tilde{K}(\omega) \tilde{F}_{tr}(\omega), \quad (6)$$

where tilde is the FT symbol. In the theory of signal processing, $\tilde{K}(\omega)$ is referred to as the transfer function of SI. Since $\tilde{K}_{\omega \rightarrow \infty}^{-1}(\omega) \rightarrow 0$, the precise true (deconvoluted) spectrum cannot be evaluated on the basis of Eq. 6. The only possibility is solving Eq. 7, which contains regularization window (filter) (W_α) [29, 31]:

$$F_{tr}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} W_\alpha(\omega) \tilde{K}^{-1}(\omega) \tilde{F}_{ms}(\omega) e^{jx\omega} d\omega, \quad (7)$$

where $j = \sqrt{-1}$. The mathematical requirements that W_α should meet are described in [31]. In particular, at infinity, W_α must decay more rapidly than the kernel.

In the simplest case of truncated inverse FT (7) [31],

$$W_\alpha^{(rect)}(\omega) = \begin{cases} 1 & |\omega| < 1/\alpha \\ 0 & |\omega| > 1/\alpha \end{cases}. \quad (8)$$

Since the inverse FT of Eq. 8 is the *sinc*-function, the corresponding regularization algorithm produces a wrong structure, i.e., side lobes. Therefore, other windows, such as Gaussian and exponential, were proposed [9, 31], which are more useful for regularization [31] because their FTs do not exhibit side lobes.

The deconvoluted spectrum may also be approximated using the following form of the inverse FT of Eq. 6 [25]:

$$F_{tr}(x) = F_{ms}(x) + \frac{1}{2\pi} \int_{-\infty}^{\infty} (\tilde{K}^{-1}(\omega) - 1) \tilde{F}_{ms}(\omega) e^{jx\omega} d\omega. \quad (9)$$

The unit subtracted in the integrand improves the deconvolution stability (9).

Substituting functional decomposition

$$\tilde{K}^{-1}(\omega) - 1 = \sum_{n=1}^N b_n \tilde{U}_n(\omega) \quad (10)$$

into Eq. 9 gives the following approximation of the true spectrum:

$$\hat{F}_{tr}(x) = F_{ms}(x) + \sum_{n=1}^N b_n \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{U}_n(\omega) \tilde{F}_{ms}(\omega) e^{jx\omega} d\omega. \quad (11)$$

If $\tilde{U}_n(\omega) = (j\omega)^n$ and $\tilde{K}(\omega)$ is an even function, then

$$\hat{F}_{tr}(x) = F_{ms}(x) - b_2 F_{ms}^{(2)}(x) + b_4 F_{ms}^{(4)}(x) - \dots \quad (12)$$

Thus, deconvolution can be considered as a sum of the spectrum and its weighted even-order derivatives. It can also be seen that the even-order DS is one of the correcting components of Eq. 12.

For example, decomposition (10) for the Gaussian kernel is

$$e^{C_2 \omega^2} - 1 \approx C_2 \omega^2 + (C_2^2/2) \omega^4, \quad (13)$$

where $C_2 = w^2/16 \ln 2 \ll 1$, and w is the full kernel width at half height.

Similarly, inverse Gaussian kernel is represented as the sum of the even-order derivatives by means of Hermite polynomials [32] (Rodrigues' formula [11]), which is the optimal decomposition of a Gaussian due to the exponential convergence rate [33].

It should be emphasized that Eq. 12 can be described as a digital filter, the coefficients being weighted sums of the even-order derivative filters. According to the terminology accepted in [15], this filter is the inverse SI-model operator.

Since the interferogram is the "raw" information of a FT instrument, deconvolution in the frequency domain is most effective in FT spectroscopy.

C. Inverse filtering in the spatial domain.

The term of *inverse filtering* for the iterative deconvolution algorithm was coined in [7], where estimating the true spectrum was considered as an iterative process:

$$(\hat{F}_{tr})_t = (\hat{F}_{tr})_{t-1} + a_t(y) (F_{ms} - (\hat{F}_{tr})_{t-1} \oplus K), \quad (14)$$

where $t=1, 2, \dots$, $a_t(y)$ is a weighting coefficient, y is the amplitude of $(\hat{F}_{tr})_{t-1}$, and $\oplus$ is the convolution symbol.

Non-stationary inverse filtering is also referred to as the SI inverse model [15]. According to this model, the true spectrum is estimated as

$$\hat{F}_{tr} = R(F_{ms}), \quad (15)$$

where R is a nonlinear operator, which can be approximated by a variety of digital filters [17-21], e.g., by a Cauchy filter [19, 20]:

$$\hat{F}_{tr}(x_i) = \left[1 + \left(\sum_{k=-K}^K a_k F_{ms}(x_{i-k}) \right)^2 \right]^{-1}, \quad (16)$$

where a_k is the k^{th} filter coefficient.

For a given SI, the coefficients of the chosen filter were estimated by minimizing the rigorous mathematical criteria at the calibration stage [15]. Calibration was performed using a stable etalon spectrum disturbed only by the instrumental function (e.g., [19]). At the validation stage, a quasi-optimal filter (a reconstruction algorithm) was chosen using the maximum accuracy criterion of the spectrum reconstruction. In our opinion, this method is the best for correcting instrumental disturbances.

Rigorous mathematical theory of inverse (or numerical, as it is referred to in [26]) filtering is based on the *eigenfunction analysis* of integral operator K ($(KF_{ms})(x)$):

$$\hat{F}_{tr}(x_i) \cong \sum_{k=0}^M \frac{(F_{ms})_k}{\lambda_k} \Psi_k(x), \quad (17)$$

where $(F_{ms})_k = \int F_{ms}(p) \Psi_k^*(p) dp$, Ψ_k , and λ_k being k^{th} eigenfunction and eigenvalue, respectively; the star denotes complex conjugation.

In contrast to decomposition of F_{ms} in a series of derivatives (Eq.12) (which may converge poorly), inverse filtering allows optimal choosing the cut-off limit (M) in Eq. 17 according to the appropriate small eigenvalue λ_M . In this way, the deconvolution stability can be significantly improved.

In some cases, when K is known *a priori*, eigenfunctions can be evaluated theoretically [23].

Deconvolution stability can also be improved using the *Principal Component Analysis* [34] (based on the same conceptions as the eigenfunction analysis) of kernel matrix K (see Eq. 4). The reconstructed matrix

$$K_{rec} = T V_{red}^T, \quad (18)$$

where $T = K V_{red}$ is the scores matrix, Matrix V_{red} is obtained by means of singular-value decomposition of matrix $K = U S V^T$ by choosing only the first M rows of matrix V . The cut-off limit (M) is calculated using the percentages of the total variance explained by each principal component of covariance matrix $K^T K$ (e.g., by the MATLAB `pcacov` function).

D. Inverse filtering in the frequency domain.

The theory and the perspectives of applying the non-stationary inverse filtering in the frequency domain are described in [27].

Super resolution in FTIR spectroscopy was achieved by reconstructing instrumentally truncated interferograms using the Gauss-Hermite decomposition [35]. This method is similar to the eigenfunction analysis, described in the previous section. It should be noted that the deconvolution problem in proton dosimetry was earlier formulated in terms of the Hermite polynomials [31], the mathematical foundation of this approach being well-known [23].

2.2. Pseudo deconvolution.

In many practical cases (e.g., in condensed-phase molecular spectroscopy [1]), the dominant line broadening is accounted for by intra- and/or intermolecular interactions in the samples under study. From the formal point of view, these interactions cause convolution of the true-line profile with a non-stationary kernel. The kernel of stationary line convolution may be described by a Gaussian function (e. g., for vibrational spectra of liquids [5] or atomic plasma spectra [3]). However, the function width is an unknown parameter. Moreover, deconvolution with this kernel may disturb a measured spectrum. Therefore, the PS technique is not applicable if the correlation between the line form parameters and the physicochemical properties of the sample under study is to be established. In this case, decomposition of a complex spectral profile into elementary components is preferable to the deconvolution method.

Instrumental calibration and deconvolution considered above are not applicable in the case of PS since instrumental line distortions are not essential. However, the reconstruction algorithms developed in [15] may be successfully used here.

If the sample parameters remain constant in the course of measurement, the measured and the true sample spectrum are similar. In this case, the aim of pseudo deconvolution is improving the resolution of the measured spectrum (making, in this way, the measured spectrum quasi ideal).

If a spectrum is superposition of approximately equal-width lines, then the "average" line FT may be used as the kernel in Eq. 6, the method being referred to as Fourier self-deconvolution (FSD) [9]. A similar approach to the deconvolution problem was based on the concept of enhancement operator [36]. The ideal enhancement operator for spectral line $f(x)$ defined as

$$E_{\beta}\{f(x)\} = f(x/\beta), \quad (19)$$

where $0 < \beta \leq 1$. It was found that $E_{\beta} \sim K^{-T_d}$ for a Gaussian line, where $T_d = 1 - \beta^2$ is the deconvolution coefficient.

As a typical example of FSD, consider a Gaussian line of unit width deconvoluted with a Gaussian kernel:

$$F_{id}(x) \sim \int_{-\infty}^{\infty} W_{\alpha}^{(rect)}(\omega) \tilde{K}^{-1}(\omega) \tilde{F}_{ms}(\omega) e^{jx\omega} d\omega, \quad (20)$$

where $\tilde{K}^{-1}(\omega) = e^{T_d \omega^2 / (16 \ln 2)}$ and $\tilde{F}_{ms}(\omega) = e^{-\omega^2 / (16 \ln 2)}$. The resolution enhancement

$$R_{en} = 1/w_d = 1/\sqrt{(1 - T_d)} = 1/\beta, \quad (21)$$

where w_d is the width of deconvoluted line.

In the limiting case of the Gaussian kernel width being very close to the width of the measured Gaussian line, $T_d \rightarrow 1$, and $R_{en} \rightarrow \infty$. The calculation results obtained using Eq. 20, with $T_d = 0.999$ and finite integration limits ($Lim = 1/\alpha$) are shown in Fig.1. Here a well-known mathematical phenomenon (described in [37]) is demonstrated, namely, the appearance of an oscillating spectrum structure (side lobes) in the case of finite integration limits due to multiplying the integrand by rectangle window $W_{\alpha}^{(rect)}(\omega)$ (8) [37].

In other words, regularization ($\alpha > 0$) suppresses the high Fourier frequencies and thus reduces the noise impact on deconvolution, but, on the other hand, it distorts the line structure by the appearance of side lobes which are negligible only if $Lim > 200$. For lower Lim values, the drawback of side lobes can be eliminated by applying apodization ("removing the foot"). According to [9, 31], an additional exponential

$$W_{\alpha}^{(exp)}(\omega) = e^{-\gamma|\omega|} \quad (22)$$

or Gaussian

$$W_{\alpha}^{(gauss)}(\omega) = e^{-0.5\gamma\omega^2} \quad (23)$$

window in the integrand of Eq. 20 [9, 31]). These windows do not produce side lobes artifacts. Windows (22) and (23) decrease the width of the Gaussian deconvolution kernel, e.g., in the latter case,

$$\tilde{K}^{-1}(\omega) = e^{(0.999 - 8\gamma \ln 2)\omega^2 / (16 \ln 2)} \quad (24)$$

Therefore T_d also decreases and so may the integration limits. On the other hand, the resolution enhancement becomes worse (Fig.1c, $T_d = 0.95$). It can be also seen (Figs.1b and 1c) that the exponential window (Eq. 22) broadens the Gaussian line wings.

A real-life measured spectrum (Eq. 20) includes random noise η :

$$\tilde{F}_{ms}(\omega) = e^{-\omega^2 / (16 \ln 2)} + \eta(\omega) \quad (25)$$

Further we suppose that the noise has zero mean value and the standard deviation ξ_{η} . Deconvolution of random noise with zero mean value

$$F_{noise}(x) \sim \int_{-\infty}^{\infty} W_{\alpha}^{(rect)}(\omega) \tilde{K}^{-1}(\omega) \eta(\omega) e^{jx\omega} d\omega \quad (26)$$

produces a wide periodical structure with negative values, as shown earlier [31] and confirmed by the results presented in Fig.2.

The frequency and the intensity of $F_{noise}(x)$ increases with the increase of the integration limits. Moreover, for large resolution enhancement, the deconvolution process becomes unstable due to the impact of variable side lobes. In other words, spectral lines and their positions may differ significantly in each new scanning. This problem can be partly solved by noise filtering, which, on the other hand, decreases spectral resolution.

The side lobes can be effectively suppressed by the smoothing the spectrum before deconvolution or by filtering in the FSD-kernel. For example, consider the modified inverse Gaussian kernel (see Eq. 13):

$$\tilde{K}^{-1}(\omega) = \exp((1 + C_2 \omega^2 + C_4 \omega^4)/(1 + k \omega^6)), \quad (27)$$

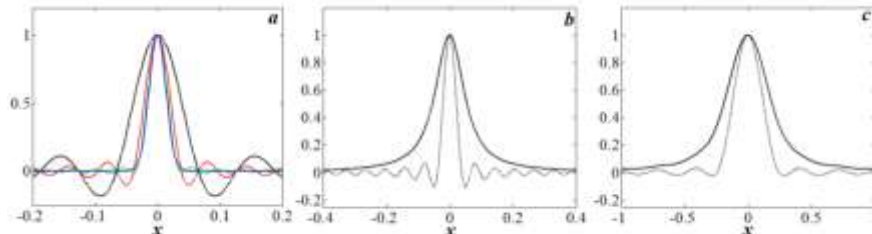
where k is the smoothing parameter. The coefficients C_2 and C_4 define the weights of the second- and forth-order derivatives in deconvoluted line.

The result of deconvolution of the unit-width Gaussian line with kernel (27) is presented in Fig.3. It can be clearly seen that the FSD quality strongly depends on the kernel parameters (particularly, on the weight of the second-order derivative), which, in turn, depend on the spectral noise and on the allowed intensity of the side lobes. Moreover, if a spectrum contents a non-zero baseline then FSD may produce artifacts [37] (Fig. 3d).

Another method used to decrease the side lobes is Tikhonov regularization in the spatial domain (Fig. 4). The results presented here demonstrate that the regularization parameter can be chosen as a compromise between the resolution enhancement and the side lobe intensities.

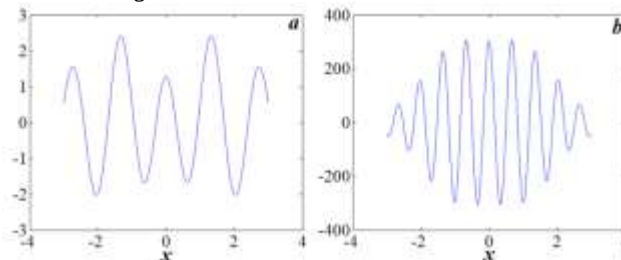
Deconvolution performed according to Eq. 12 was studied in 1990th using model spectra which consisted of equal-width lines (see [39] and references therein). The expression for resolution enhancement obtained theoretically [36] confirmed the practically observed increase of the resolution power of the method in the case of using higher-order derivatives (compare Figs. 5b and 5c). The increased weight of the forth-order derivative improves the resolution at the expense of larger side lobe intensities (Fig. 5c). The outside symmetrical side lobes observed in Figs. 5b and 5c are a typical feature of deconvoluted lines, while the internal side lobes are not seen because they overlap with the main line peaks. If the line widths are different, the side lobes appear asymmetrically (Fig. 6, where R and r are the relative intensity and the relative width of the second component, respectively). Therefore, the kernel width should be chosen in accordance with the narrowest line, the wider line shrinking being, in this case, lower.

Figure 1. Fourier self-deconvolution of a noise-free Gaussian line.



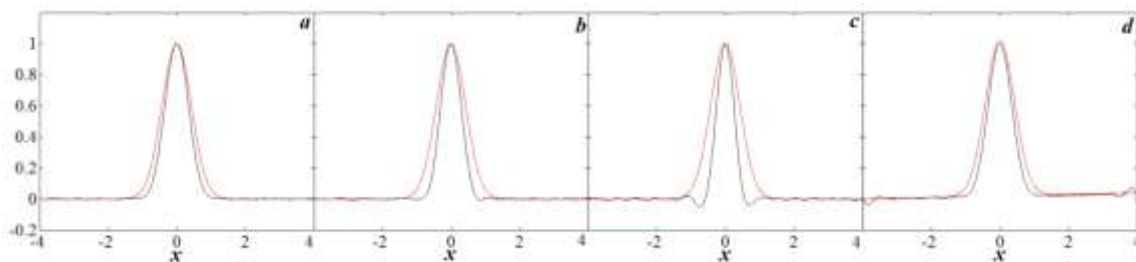
(a) Lim : 50 (black), 100 (red), 150 (green), and 200 (blue); $\gamma = 0$. (b) $Lim = 100$, $\gamma = 0$ (...) and 0.05 (-). (c) $Lim = 20$, $\gamma = 0$ (...) and 0.12 (-).

Figure 2. Fourier self-deconvolution of noise.



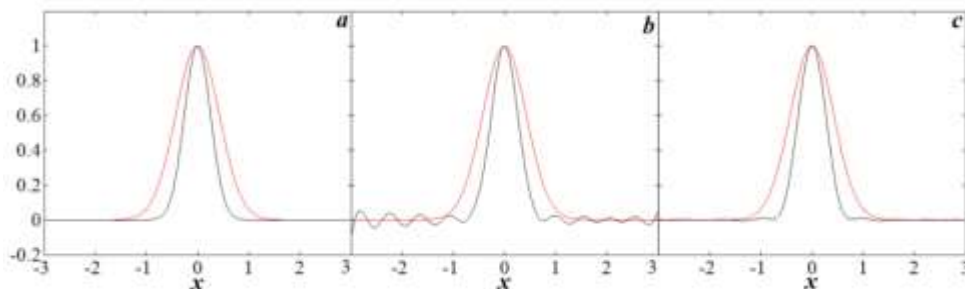
$\xi_\eta = 10^{-3}$, $T_d = 0.80$, $Lim = 5$ (a) and 10 (b).

Figure 3. Deconvolution of a Gaussian line with a FSD kernel.



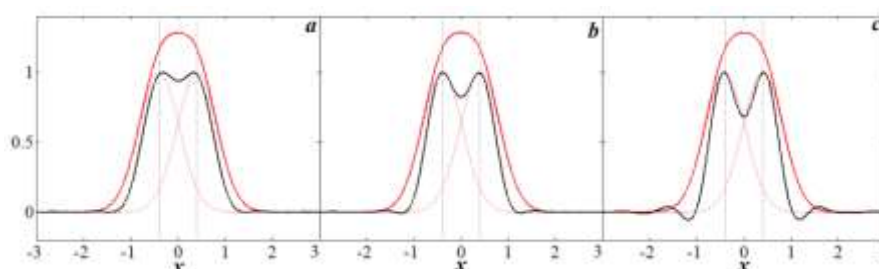
$\xi_\eta = 0.002$, $C_4 = 10^{-6}$, $k = 10^{-7}$. (a) $C_2 = 0.02$, $R_{en} = 1.22$. (b) $C_2 = 0.03$, $R_{en} = 1.43$. (c) $C_2 = 0.04$, $R_{en} = 1.71$. (d) $C_2 = 0.02$, baseline is present.

Figure 4. Deconvolution of Gaussian line using Tikhonov regularization



$T_d = 0.64$. (a) $\xi_\eta = 0$, $\alpha = 10^{-5}$, $R_{en} = 1.66$. (b) $\xi_\eta = 10^{-3}$, $\alpha = 0.01$, $R_{en} = 1.65$. (c) $\xi_\eta = 10^{-3}$, $\alpha = 0.9$, $R_{en} = 1.59$.

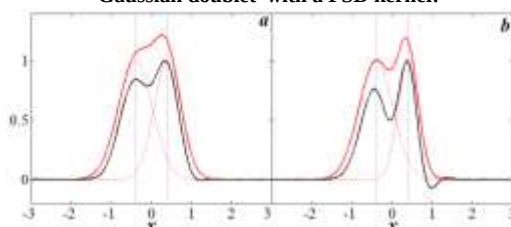
Figure 5. Deconvolution of a symmetrical Gaussian doublet with a FSD kernel.



$\xi_\eta = 0.002$. (a) $C_2 = 0.04, C_4 = 10^{-6}, k = 10^{-6}$. (b) $C_2 = 0.05, C_4 = 10^{-4}, k = 10^{-6}$. (c) $C_2 = 0.05, C_4 = 7 \times 10^{-4}, k = 3 \times 10^{-6}$.

The set of spectra presented in Fig. 7 illustrates the distortion of a weak broad line by side lobes, which appear as a result of over-deconvolution. Since the wide line and the wings of the narrow line merge, side lobes are not

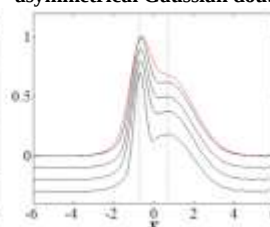
Figure 6. Deconvolution of an asymmetrical Gaussian doublet with a FSD kernel.



$\xi_\eta = 0.002, C_2 = 0.025, C_4 = 10^{-6}, k = 10^{-7}$.

$R = 1, r = 0.8$ (a) and 0.6 (b).

Figure 7. Over-deconvolution of an asymmetrical Gaussian doublet.



$R = 1, r = 3. T_d = 0.4, 0.5, 0.6 \text{ and } 0.9$,

from top to bottom. Clearly visible next to the peaks. However, it can be seen that the weak broad line is distorted and its maximum position is shifted. This observation is confirmed by a numerical experiment, in which the peak positions were estimated after adding a noise to a deconvoluted spectrum. This procedure was repeated 100 times and the relative shifts of the peak positions were calculated. It was found that with the increase of T_d , the relative shifts decrease to a certain threshold and then anomalous changes of the shifts occur, which are indicative of over-deconvolution (Table). If the precise kernel form is unknown, deconvolution produces an intensive wrong line structure, which is similar to the satellites of the second-order derivative (Fig. 8).

In conclusion, it should be noted that iterative self-deconvolution in the spatial domain of X-ray fluorescence spectra was performed using a non-linear digital filter [40].

2.3. Comparison of deconvolution algorithms.

When comparing different deconvolution algorithms and selecting the algorithm appropriate for a particular problem, several interrelated criteria should be taken into account, namely, resolution enhancement, relative intensities of the side lobes, and the computation time. Generally speaking, in instrumental deconvolution, the inverse model is preferable to the forward one, while in pseudo deconvolution, the model should be chosen also with regard to the essential features of the problem under study.

In the measurements of spectral peak positions, the resolution enhancement must meet the condition of acceptable peak maximum shifts from their precise values [41]. In the measurements of line intensities, line overlapping must be negligible. However, due to the high resolution power of the deconvolution algorithm, artificial side lobe structures may still be produced and erroneous results obtained. Small computation time is essential for on-line analytical control of technological processes. Thus, it is clear that there does not exist any general solution for all deconvolution problems, only a compromise being possible in each particular case.

For example, consider a symmetrical Gaussian doublet which was deconvoluted by the Tikhonov regularization method, including two different preprocessing steps. In the first case, the doublet was smoothed (Fig. 9a), while in the second case, the Gaussian kernel was reconstructed according to Eq. 18, using a limited number of the principal components (Fig. 9b). The plots clearly show that better resolution is obtained by the second approach, which, on the other hand, is significantly more time-consuming than the smoothing procedure.

In the second example, polyester reflection spectra [42] were deconvoluted using the above two preprocessing methods with subsequent Tikhonov regularization (Fig. 10). The spectra are very similar in both cases; however, the deconvolution process with preliminary smoothing is much faster than with kernel reconstruction.

It has already been mentioned above that a non-zero baseline at the edges of a spectral curve produces oscillations. These oscillations are not observed in Fig. 9, where such baseline is absent. However, they are present in the deconvoluted polyester spectrum which disturbed edges are not shown in Fig. 10.

Using deconvolution of a known convoluted spectrum, it is possible to study the properties of deconvolution algorithms and choose their optimal parameters. An example is given in Fig. 11, which illustrates Tikhonov-based deconvolution of a symmetrical Lorentzian doublet convoluted with a Gaussian kernel. Noise was added

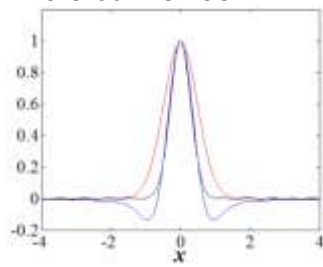
to the convoluted doublet. This numerical experiment allows finding a compromise between the resolution loss in the deconvoluted doublet (relative to the original doublet before convolution) and the acceptable level of side lobes. Comparison of different deconvolution algorithms has always been performed using an extremely limited number of synthesized and/or real-life spectra. Therefore, it is often quite difficult to estimate how close the developed algorithm is to the "best" one. In our opinion, each algorithm should be compared with the quasi optimal one for deconvolution of the validation set consisting of the typical spectra for the problem under study. This set may be composed of Gaussian, Lorentzian, or Voigt multiplets, with widely ranging parameters. The approximate values of these parameters can be readily obtained from the spectra deconvoluted by a quasi-optimal method. As an example, in Fig.12, the FSD of an "ideal" noise-free Gaussian line (Eq. 20) is compared with a more real-life case of the same line with added noise, the FSD being performed in a limited range of integration ($Lim = 10$). However, in the latter case, the wide wings of the line are rarely observed in practice. Therefore, in the second example (Fig. 13), a Gaussian line with truncated wings ($Lim = 3$) was deconvoluted by Tikhonov method. The resolution enhancement (R_{en}) was calculated using Eq. 21. The intensity of the side lobes was evaluated on the basis of the standard deviation (ξ_w) of the Gaussian wings (Fig. 13b). The above examples (Figs. 12 and 13) demonstrate that truncation significantly decreases the R_{en} values. Thus the optimal T_d value should be chosen as a compromise between the maximum resolution enhancement and the acceptable level of side lobes

Table. Relative peak shifts (%) for a deconvoluted asymmetrical Gaussian doublet components in the case of Tikhonov regularization.

T_d							
0.4		0.5		0.6		0.9	
5.2±0.03	-3.2±0.20	4.4±0.03	-1.4±0.3	3.6±0.03	-0.7±0.4	5.2±0.03	6.3±0.5

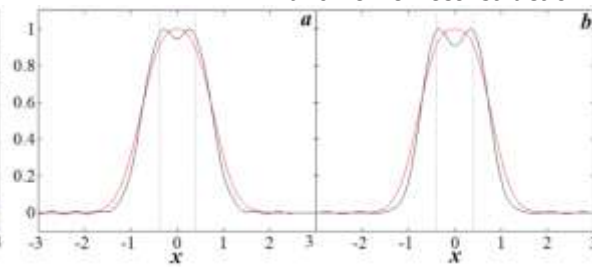
$\xi_\eta = 0.001, R = 1, r = 3$. Left and right columns correspond to the left and right doublet components, respectively.

Figure 8. Deconvolution of a Gaussian line with Gaussian and Lorentzian kernels



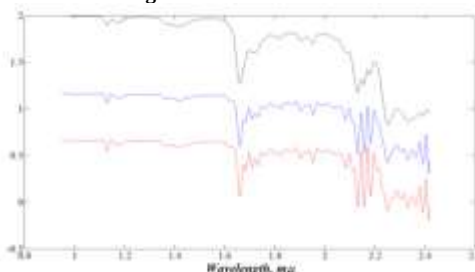
$\xi_\eta = 0.001, T_d = 0.8$. Gaussian (black) and Lorentzian (blue) kernel

Figure 9. Deconvolution of a Gaussian doublet using Tikhonov regularization with preliminary smoothing and kernel reconstruction



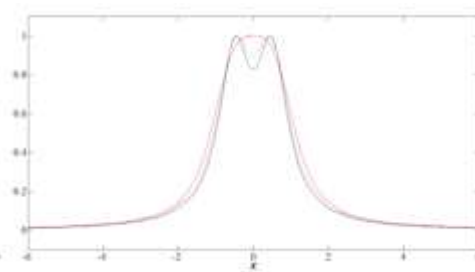
$\xi_\eta = 0.001, T_d = 0.4$. Preprocessing: smoothing (a) and kernel reconstruction (b)

Figure 10. Deconvolution of a polyester reflection spectrum using Tikhonov regularization with preliminary smoothing and kernel reconstruction.



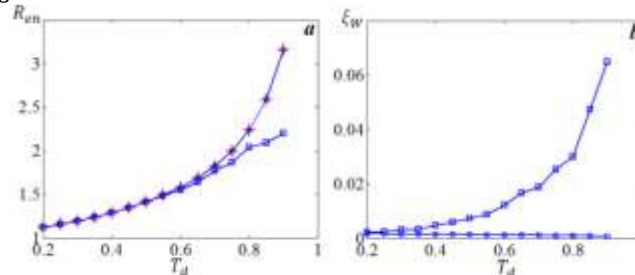
Pre-processing: (blue) smoothing and (red) kernel reconstruction

Figure 11. Tikhonov-based deconvolution of a Lorentzian doublet convoluted with a Gaussian kernel.



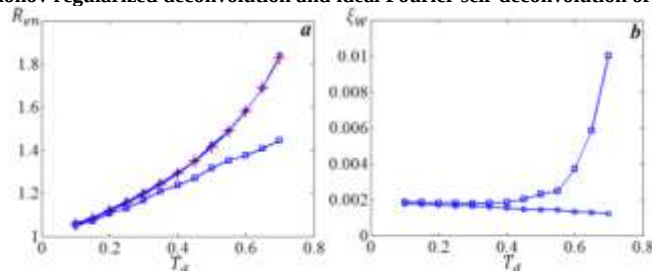
Doublets: (black) original (black), (red) convoluted, and (dotted line) deconvoluted.

Figure 12. Real-life and the ideal Fourier self-deconvolution of a Gaussian line.



(*) Theoretical R_{en} values; (o) $\xi_\eta = 0, Lim = 50$; (□) $\xi_\eta = 10^{-3}, Lim = 10$.

Figure 13. Tikhonov regularized deconvolution and ideal Fourier self-deconvolution of a Gaussian line.



(+) Theoretical R_{en} values. (o) Ideal FSD, $\xi_\eta = 0, Lim = 50$; ($\square$) Tikhonov method, $\xi_\eta = 10^{-3}$.

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