



Use of a hypothetically optimal non-recursive digital smoothing filter for comparative study of signal denoising methods in analytical chemistry

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Abstract: *We developed a hypothetically optimal non-recursive digital smoothing filter which minimises the sum of the squared norms of the residuals (between true and smoothed signals) and of the smoothed noise. It has been proven theoretically that the optimal smoothing filter of constant and linear signals is the moving average filter. It was found that Savitzky - Goley and Fourier filters have near-optimal smoothing properties for the white and pink noises.*

Keywords: *smoothing; analytical signal; digital filters; Savitzky-Goley; Fourier transform; white and pink noise.*

I. Introduction

Measurements of any analytical instrumental data are influenced by the presence of the random and of the systematic errors [1-4]. While the systematic errors can be decreased to be negligible by improving the instrument and the measurement process, the random ones cannot be eliminated totally in principle; they only can be decreased by improving the measurement procedure or by mathematical treatment of the obtained results. However, the error elimination process can cause distortion of the true value to be measured.

If spectral instrument and the sample under study are very stable (there is no drift of the instrumental and sample parameters) then the signal-to-noise ratio may be significantly improved by averaging of sequential repetitions of the measurements. However, this procedure is not always possible. Moreover, it may be very time consuming. Therefore, the emergence of computer enhanced analytical instruments has stimulated the development of numerical methods for data smoothing.

The most popular smoothing filters used in analytical applications are Savitzky - Golay polynomial filters (SG) [5]. These least squares filters, well-known in mathematics, have a very long history [6, 7]. Efficient methods of computation of SG-filters were suggested [8-11] and their filtering properties were studied [9, 12-14]. Polynomial smoothing filters were also improved by Tikhonov (ridge) regularization [15-17] (the old version was named as "A method of graduation based on probability" [6] or "penalized least squares"). Chebyshev filters based on the minimax criterion were used in spectroscopy [20, 21]. Classical Finite Impulse Response (FIR) filters [20, 21] and adaptive techniques [22, 23] were taken from the Digital Signal Processing [24].

In parallel, spline [25], Fourier [26-28] and wavelet smoothing [29, 30] methods were intensively applied to analytical measurements. Matrix method based on the singular value decomposition was suggested by [31, 32]. "Exotic" Kahrnunen-Loève Transform was used by [33]. In more sophisticated method [34] the structure of the noise data was taken into account for implementation of smoothing procedure

Smoothing is the important part of the pre-processing in the multivariate calibration [35]. The possible pitfalls of applying this procedure [36] are theoretically related to the smoothing in statistics [37].

There is not perfect smoothing method applicable to all numerical data since the quality of the processing depends on the form of the noisy signal, on the type of the noise and on the signal-to-noise ratio. Being ill-posed inverse problem [38] efficient smoothing requires additional information about the signal and the noise for choosing quasi optimal parameters of the smoothing procedure, e.g., the polynomial power and the length of polynomial filters [9], the regularization parameter for the penalized least squares [17] and Fourier smoothing [27], the cut-off frequency of FIR filters [23], etc. However, these parameters defining the smoothing quality are based on some criterion (a global minimum of the objective function [39]). Generally, the objective function is defined as the weighted sum of the goodness-of-fit measure and the "roughness" of the smoothed signals [16-18]. The least squares goodness-of-fit measure is equal to the squared Euclidean norm of the discrepancies between the measured and the smoothed signal. The weighting factor is the regularization parameter. In the partial case of SG filter the norm is defined on the piece of data which length is equal to the filter length and the regularization parameter is zero [5].

Choosing of the quasi optimal parameters of smoothing algorithms was comprehensively discussed and illustrated by numerous examples. However, analysis of published materials clearly shows that, usually, the visual quality of the smoothed noisy signals has been considered as "the best proof" of the smoothing quality of numerical algorithm (e.g., [32]).

Suppose that the quasi optimal parameters of a given digital smoothing method applied to a given noisy signal have been well established. Then the following question arises: "How close the smoothing quality to the theoretically best quality obtained by a hypothetically perfect method of smoothing?"

The present study will answer the question posed. As a hypothetically perfect smoother we used a theoretically optimal non-recursive digital smoothing filter applied to a given noise-free analytical signal corrupted by additive noise (independent on the signal) with zero mean and known dispersion. The white and the pink noises were taken. The objective function was defined as the sum of the measures of the signal distortion and of the noise passed through the filter. Unlike SG method the signal distortion was estimated as the squared Euclidean norm of the discrepancies between the non-distorted and the smoothed signal in the all analytical points (except some start and end points; the same is true for the noise estimation).

We compared the minimum values of the objective function obtained for the theoretically optimal and for the SG and Fourier smoothing filters. Symmetrical Gaussian doublet was taken as a model of the noise-free signal. Surprisingly, it was found the SG filter is the most efficient for smoothing of a very large set of simulated and real noisy spectra. However, all data is not included in the paper because its volume is limited.

In what follows, for the sake of simplicity, the term "peak" is used instead of terms "line" and "band". Scalar quantities will be denoted by lowercase and uppercase letters, matrix and vectors by uppercase and lowercase bold letters, respectively. All vectors are given as row vectors. The symbol $\| \cdot \|$ represents the Euclidean norm. T is the transpose symbol. All calculations were performed and the plots were built using functions available with MATLAB software.

II. Theory

Let the measured analytical signal be: $\mathbf{F}_m = \mathbf{F} + \boldsymbol{\eta}$, (1)

where the components of the vector $\mathbf{F}$: $f_i, i = 1, 2, \dots, L$ are obtained by sampling on the uniform grid with the step h of the x -axis, $\boldsymbol{\eta} = \{\eta_i\}$ is the normal noise (independent on $\mathbf{F}$) with a mean of zero; the components η_i are uncorrelated and have the same standard deviation σ .

Suppose that $\mathbf{F}_m$ is smoothed by the linear symmetrical non-recursive digital filter. The vector of the filter coefficients $\mathbf{w} = \{w_j\}$, $j = 1, 2, \dots, N = 2m + 1$, and $w_k = w_{N-k+1}$, $k = 1, 2, \dots, m$.

Our goal is to found the optimal set of the N coefficients w_j which minimizes the object function:

$$\theta = \|\mathbf{F}_{red} - \mathbf{F}_m \mathbf{W}\|^2, \quad (2)$$

where $\mathbf{F}_{red}$ is defined in the range: $(m + 1, m + 2, \dots, L - m)$.

$$\mathbf{W} = \begin{bmatrix} w_1 & 0 & \dots & 0 \\ w_2 & w_1 & \dots & \vdots \\ \vdots & w_2 & \dots & 0 \\ w_N & \vdots & \dots & w_1 \\ 0 & w_N & \dots & w_2 \\ \vdots & \vdots & \dots & \vdots \\ 0 & 0 & \dots & w_N \end{bmatrix}$$

Substituting (1) into (2) and ignoring the term $2(\mathbf{F}_{red} - \mathbf{F}_m)^T \boldsymbol{\eta} \mathbf{W}$ which average value is negligible compared to another terms, we have

$$\theta = \|\mathbf{F}_{red} - \mathbf{F}_m \mathbf{W}\|^2 + \|\boldsymbol{\eta} \mathbf{W}\|^2 \quad (3)$$

Since the average value $\overline{\eta_i \eta_j} = \begin{cases} \sigma^2, & i = j \\ 0, & i \neq j \end{cases}$

$$\|\boldsymbol{\eta} \mathbf{W}\|^2 = \boldsymbol{\Phi}_\eta \mathbf{w}^T \mathbf{w} \boldsymbol{\Phi}_\eta^T = (L - N + 1) \sigma^2 \|\mathbf{w}\|^2, \quad (4)$$

$$\text{where } \boldsymbol{\Phi}_\eta = \begin{bmatrix} \eta_1 & \eta_2 & \dots & \eta_N \\ \eta_2 & \eta_3 & \dots & \eta_{N+1} \\ \vdots & \vdots & \vdots & \vdots \\ \eta_{L-N+1} & \eta_{L-N+2} & \dots & \eta_L \end{bmatrix}$$

In what follows we will suppose that in the last and the first m points $f_i \ll \sigma$.

The column vector of the derivatives of θ over the coefficients w_j :

$$\boldsymbol{\theta}'_w = -2\boldsymbol{\Phi}_F^T (\mathbf{F}_{red} - \mathbf{F}_m \mathbf{W})^T + 2(L - N + 1) \sigma^2 \mathbf{w}^T \mathbf{I}, \quad (5)$$

where matrix $\boldsymbol{\Phi}_F$ has the structure of the matrix $\boldsymbol{\Phi}_\eta$, $\mathbf{I}$ is the identity matrix ($N \times N$).

Since all elements of the vector of the second order derivative $\boldsymbol{\theta}''_w$ are positive, the zeroes of $\boldsymbol{\theta}'_w$ are correspond to the minimum of the objective function over filter coefficients.

Substituting $\mathbf{F}_m \mathbf{W} = \boldsymbol{\Phi}_F \mathbf{w}^T$ into (5) which is equal to the zero vector in the minimum of the objective function, we have:

$$(\boldsymbol{\Phi}_F^T \boldsymbol{\Phi}_F + (L - N + 1) \sigma^2 \mathbf{I}) \mathbf{w}^T = \boldsymbol{\Phi}_F^T \mathbf{F}_{red}^T \quad (6)$$

When $\sigma = 0$ the trivial solution of (6) $\boldsymbol{\Phi}_F \mathbf{w}^T = \mathbf{F}_{red}^T$ $w_i = \begin{cases} 1, & i = m + 1 \\ 0, & i \neq m + 1 \end{cases}$ has no practical interest.

Generally, the solution of (6) is

$$\mathbf{w}^T = (\Phi_F^T \Phi_F + (L - N + 1)\sigma^2 \mathbf{I})^{-1} \Phi_F^T \mathbf{F}_{red}^T \quad (7)$$

Matrix $\Phi_F^T \Phi_F$ is badly conditioned. Matrix $(L - N + 1)\sigma^2 \mathbf{I}$ is the regularization term in the matrix inverse.

Equation (7) can be analytically solved only in some particular cases (see below). Here we only note that the coefficients of the optimal filter are obtained by the convolution of the true analytical signal with the matrix kernel $(\Phi_F^T \Phi_F + (L - N + 1)\sigma^2 \mathbf{I})^{-1} \Phi_F^T$. The kernel depends on the analytical signal and on the dispersion of the noise. The convolution is performed in the limits of the filter width.

Analytical solution of (7) for $f_i = 1$ ($i = 1, \dots, L$) was obtained using elegant inversion procedure suggested by J. Falta [40]:

$$\left(\frac{\Phi_F^T \Phi_F}{L - N + 1} + \sigma^2 \mathbf{I} \right)^{-1} = \frac{1}{\sigma^2(N + \sigma^2)} \begin{vmatrix} N - 1 + \sigma^2 & -1 & \cdots & -1 \\ -1 & N - 1 + \sigma^2 & \cdots & -1 \\ \vdots & \vdots & \ddots & \vdots \\ -1 & -1 & \cdots & N - 1 + \sigma^2 \end{vmatrix}$$

Substituting the last equation in (7) we have:

$$\mathbf{w} = 1/(N + \sigma^2) [1, 1, \dots, 1] \quad (8)$$

Usually σ^2 is negligible compared to N , therefore the filter (8) is the moving average.

The analytical solution of inverse matrix (7) in the linear case $f_i = f_0 + hi$ was obtained by J. Domsta [40] (see Appendix).

III. Computer modeling

Analytical signal was modelled by the symmetrical Gaussian doublet (Fig. 1):

$$\mathbf{F}_G = \exp[-4\ln 2(\mathbf{x} + d)^2] + \exp[-4\ln 2(\mathbf{x} - d)^2], \quad (9)$$

where the components of vector $\mathbf{x}$ were taken uniformly in the range $[-6, 6]$ with the step 0.01, $d = 0.47$ is the half-peak separation. In order to completely eliminate the effect of loss of the start and the end points while digital smoothing, the object function θ (3) was estimated in the range $[-1.5, 1.5]$. The length of the reduced range was $L_{red} = 301$ points. At the edges of this interval the intensity of the doublet was less than 0.2% of its maximum value. So, the doublet wings were emerged into the noise which standard deviation (σ) was taken as 0.005, 0.01, 0.02 and 0.05.

The signal smoothed in the Fourier domain:

$$\mathbf{F}_{G_{sm}} = \text{real}\{IFT[FT(\mathbf{F}_G) * \text{Filter}(\omega)]\}, \quad (10)$$

where *real* is a real part of Fourier transform (*FT*), *IFT* is inverse *FT*, $\text{Filter}(\omega) = 1/(1 + \lambda\omega^6)$, λ is the regularization constant, ω is the angular frequency.

Pink noise was generated using Matlab program [41].

For a given m and λ the same noisy signal was smoothed using SG, optimal and Fourier filters. Processing with new regenerated noise was repeated 20 times and the average error $\varepsilon = \sqrt{\theta/L_{red}}$ and its standard deviation (σ_ε) were estimated for each smoothing method. Due to the same noise component the errors obtained by these methods were strongly correlated. Therefore, three σ_ε values were very close to each other. The radius of the 95% confidence interval of the ε ($\Delta\varepsilon$) was calculated using maximum σ_ε . Error dependencies $\varepsilon(m)$ for SG and optimal filters and $\varepsilon(\lambda)$ for Fourier method were estimated.

Figure 1 Gaussian doublet

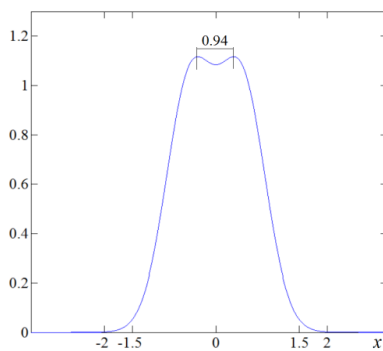
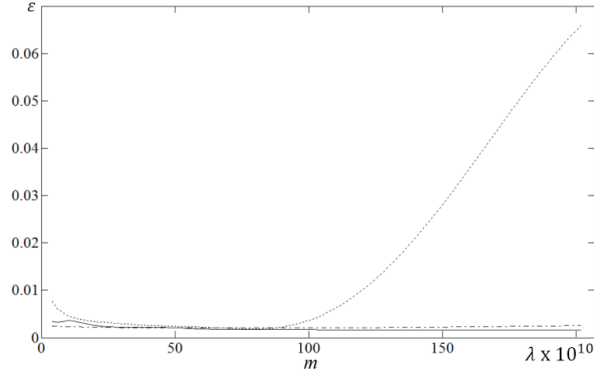


Figure 2 Error dependencies for the smoothing filters



Dotted, solid and dash-dotted line for SG (power 6), optimal and Fourier filters, respectively. White noise, $\sigma = 0.01$.

IV. Results and Discussion

The following conclusion can be drawn from the data which are summarized in Fig. 2 and Table 1.

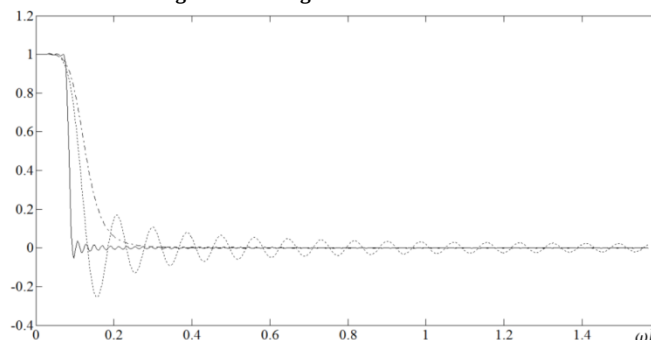
1. If the power of SG filter increases than the error ε_{min} decreases but the filter width (m_{opt}) increases [9].

2. For the optimal filter $\varepsilon_{min_{opt}} \leq \varepsilon_{min}$. It was found that this is a valid inequality for other filters including the non-recursive filters [16, 18, 19] which applications were not described in the article. For this study a family of the Chebyshev filters with variable width was built. Also we found that this is a valid inequality for a large set of simulated and real noisy spectra.
3. For the pink noise $\varepsilon_{min_{pink}}$ is significantly large that that for the white noise $\varepsilon_{min_{white}}$.
4. $\varepsilon_{min_{opt}}$ is approximately proportional to the standard deviation of the noise σ .
5. If the width of the optimal filter increases then its frequency characteristic becomes close to rectangle (Fig. 3) which Fourier transform (the impulse characteristic of the filter) resembles $sinc(x) = \sin(x)/x$ function.

Table 1 Optimal parameters of smoothing filters using for denoising of the Gaussian doublet

Noise	Optimal values	σ x 10 ³	Filter					max $\Delta \varepsilon_{min}$
			SG : power			Optimal	Fourier	
			2	4	6			
white	$\varepsilon_{min},$ x 10 ⁴	5	12	10	9.0	8.0	10.0	0.9
		10	22	19	18	16	19.0	1.8
		20	42	39	37	34	38	4
		50	85	80	77	70	79	9
	m_{opt} and α_{opt} x 10 ⁹	5	22	43	68	292	2.6	-
		10	24	49	74	302	4.8	
		20	30	55	82	290	9.5	
		50	38	67	96	287	28	
pink	$\varepsilon_{min},$ x 10 ⁴	5	33	31	31	31	31	2
		10	62	61	60	57	61	7
		20	133	130	129	129	130	11
		50	306	292	291	291	292	77
	m_{opt} and α_{opt} x 10 ⁹	5	26	49	76	325	5.8	-
		10	30	55	82	262	11	
		20	38	65	94	160	25	
		50	46	79	110	141	40	

Figure 3 Frequency characteristics of the optimal filters using for denoising of the Gaussian doublet



$\sigma = 0.01$. SG (power=6, m=74), optimal (m=302) and Fourier ($\lambda = 5 \times 10^{-9}$): dotted, solid and dash-dotted line, respectively.

V. Conclusion

Numerical data obtained by computer modeling clearly showed that SG and Fourier filters have near-optimal smoothing properties. However, the optimal parameters of these filters (in context with the article) depend on the "pure" unknown measurement signal (free of noise) and on the noise properties. Generally speaking, since the solution to the optimal smoothing problem contains so many unknowns it requires the correct initial conditions for further discussion, that is, the optimal smoothing criteria, the signal which must be smoothed and the noise characteristics.

VI. Acknowledgements

The author grateful to prof. J. Domsta (University of Applied Sciences, Elblag, Poland) and to J. Falta (Czech Technical University, Prague) for solving some mathematical problems cited in the article.

VII. APPENDIX

Estimation of the optimal filter for a linear signal

Given matrix $\Phi_f = \begin{bmatrix} f_1 & f_2 & \cdots & f_N \\ f_2 & f_3 & \cdots & f_{N+1} \\ \vdots & \vdots & \vdots & \vdots \\ f_{L_N} & f_{L_N+1} & \cdots & f_L \end{bmatrix}$, where $f_i = f_0 + hi$, $L_N = L - N + 1$.

For simplicity consider case $h = 1$.

According to the definition suggested by J. Domsta [40]:

$\mathbf{M} = \Phi_f^T \Phi_f + z\mathbf{I}$, where $z = L_N \sigma^2$, $\mathbf{I}$ is the identity matrix.

$\Phi_f^T \Phi_f = (a\mathbf{U} + b\mathbf{V})(a\mathbf{U} + b\mathbf{V})^T + c^2 \mathbf{U}\mathbf{U}^T$,

where $a = \epsilon_0 \sqrt{NL_N}$, $\epsilon_0 = k_0 + j_0 - 1$, $k_0 = (1 + N)/2$, $j_0 = (1 + L_N)/2$, $b = h\sqrt{K_2 L_N}$, $c = h\sqrt{Nj_2}$,

$K_2 = \mathbf{v}_k^T \mathbf{v}_k$, $\mathbf{v}_k = \begin{bmatrix} 1 \\ 2 \\ \vdots \\ N \end{bmatrix} - k_0 \mathbf{1}_N$, $\mathbf{1}_N = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix}$, $c = h\sqrt{j_2 N}$, $J_2 = \mathbf{v}_j^T \mathbf{v}_j$, $\mathbf{v}_j = \begin{bmatrix} 1 \\ 2 \\ \vdots \\ L_N \end{bmatrix} - k_0 \mathbf{1}_{L_N}$, $\mathbf{U} = \mathbf{1}_N / \sqrt{N}$, $\mathbf{V} = \mathbf{1}_{L_N} / \sqrt{L_N}$.

Inverse matrix [40]:

$\mathbf{M}^{-1} = (1/z)(\mathbf{I} - \mathbf{U}\mathbf{U}^T - \mathbf{V}\mathbf{V}^T) + \mathbf{O}_1 + \mathbf{O}_2 - \mathbf{O}_3$,

where $\mathbf{O}_1 = R_z(1,1)\mathbf{U}\mathbf{U}^T$, $\mathbf{O}_2 = R_z(1,2)(\mathbf{U}\mathbf{V}^T + \mathbf{V}\mathbf{U}^T) + R_z(2,2)\mathbf{I}$, $\mathbf{O}_3 = R_z(2,2)(\mathbf{I} - \mathbf{V}\mathbf{V}^T)$

$R_z = \mathbf{Q}_z / \det \mathbf{Q}_z$, $\mathbf{Q}_z = \begin{bmatrix} b^2 + z & -ab \\ -ab & a^2 + b^2 + z \end{bmatrix}$.

We found that although $1/z$ is very large the terms $\mathbf{O}_i$ cannot be neglected.

According to (7):

$\mathbf{w}^T = (1/z)(\mathbf{I} - \mathbf{U}\mathbf{U}^T - \mathbf{V}\mathbf{V}^T + \mathbf{O}_1 + \mathbf{O}_2 - \mathbf{O}_3)\mathbf{T}$, (A1)

where $\mathbf{T} = \Phi_f^T \mathbf{F}_{red}^T$.

In what follow we will proof that all components of the vector $\mathbf{w}^T$ are constants.

Being normalized to the unit sum these components give the coefficients of the moving average filter. Therefore the values of these constants are not important.

The i^{th} component of the vector $\mathbf{T}$:

$T_i = \sum_{k=1}^{L_N} [k + (i - 1)][k + (N - 1)/2] = T_1 + (i - 1)\Delta T$,

where $T_1 = (L_N/2)(L_N + 1)[(2L_N + 1)/3 + (N - 1)/2]$, $\Delta T = (L_N/2)(L_N + N)$.

Consider impact of the terms $(\mathbf{I} - \mathbf{U}\mathbf{U}^T - \mathbf{V}\mathbf{V}^T + \mathbf{O}_1 + \mathbf{O}_2 - \mathbf{O}_3)$ (A1) on the vector $\mathbf{w}^T$. Since all components of the matrix $\mathbf{U}\mathbf{U}^T$ are constants $(1/N)$ all components of the vector $\mathbf{U}\mathbf{U}^T \mathbf{T}$ are also constants. This result is correct for the term $\mathbf{O}_1 \mathbf{T}$.

The i^{th} component of the vector $\mathbf{Y} = (\mathbf{I} - \mathbf{V}\mathbf{V}^T)\mathbf{T}$

$Y_i = T_i - \{[i - (N + 1)/2]/K_2\} \sum_{j=1}^N [j - (N + 1)/2] [T_1 + (j - 1)\Delta T] =$

$T_i - [i - (N + 1)/2]\Delta T(N/12)(N^2 - 1)/K_2 = T_1 - [(N + 3)/2]\Delta T$ does depend on i . This result is correct for the vector $\mathbf{O}_3 \mathbf{T}$.

The vector: $\mathbf{Z} = \mathbf{O}_2 \mathbf{T} = R_z(1,2)(\mathbf{U}\mathbf{V}^T + \mathbf{V}\mathbf{U}^T + \mathbf{I})\mathbf{T} + [R_z(2,2) - R_z(1,2)]\mathbf{I}\mathbf{T} = \mathbf{Z}_1 + \mathbf{Z}_2$,

where $\mathbf{Z}_1 = R_z(1,2)(\mathbf{U}\mathbf{V}^T + \mathbf{V}\mathbf{U}^T + \mathbf{I})\mathbf{T}$, $\mathbf{Z}_2 = [R_z(2,2) - R_z(1,2)]\mathbf{I}\mathbf{T}$.

Since all rows of the both matrices

$$\mathbf{U}\mathbf{V}^T = (1/\sqrt{NK_2}) \left\{ \begin{bmatrix} 1 & 2 & \cdots & N \\ 1 & 2 & \cdots & N \\ \vdots & \vdots & \vdots & \vdots \\ 1 & 2 & \cdots & N \end{bmatrix} - k_0 \begin{bmatrix} 1 & 1 & \cdots & 1 \\ 1 & 1 & \cdots & 1 \\ \vdots & \vdots & \vdots & \vdots \\ 1 & 1 & \cdots & 1 \end{bmatrix} \right\}$$

and $\mathbf{V}\mathbf{U}^T = (\mathbf{U}\mathbf{V}^T)^T$ are the identical, vector $\mathbf{Z}_1$ also contains identical components.

Since T_i does not depend on i , vector $\mathbf{Z}_2$ also contains identical components.

So we conclude that the moving average filter was obtained for the linear signal.

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