Journal of the Korean Vacuum Society
Vol. 5, No. 2, June 1996, pp. 99~106

Application of Regularization Method to Angle-resolved XPS Data

Chul-Un Ro

Department of Chemistry and Interdisciplinary Research Center in Physical Science, Hallym University, Chunchon, 200-702, Korea
(Received January 17, 1996)

각분해X-선광전자분광법 데이터 분석을 위한 regularization 방법의 응용

노 철 언

한림대학교 화학과 및 이화학학제간연구센타
(1996년 1월 17일 접수)

Abstract – Two types of regularization method (singular system and HMP approaches) for generating depth-concentration profiles from angle-resolved XPS data were evaluated. Both approaches showed qualitatively similar results although they employed different numerical algorithms. The application of the regularization method to simulated data demonstrates its excellent utility for the complex depth profile system. It includes the stable restoration of the depth-concentration profiles from the data with considerable random error and the self choice of smoothing parameter that is imperative for the successful application of the regularization method. The self choice of smoothing parameter is based on generalized cross-validation method which lets the data themselves choose the optimal value of the parameter.

요 약 – 각분해X-선광전자분광법 데이터로부터 화학종의 깊이분포에 대한 정보를 얻기 위한 두가지 종류의 regularization 방법 (singular system과 HMP 방법)을 연구하였다. 두 방법은 매우 다른 알고리즘을 채택하고 있지만 정성적으로 유사한 결과를 보였다. 시뮬레이션을 통하여 ARXPS 데이터에 regularization 방법을 적용하였을 때 복잡한 형태의 깊이분포를 가진 시료에 대하여 유용함을 알 수 있었다. 이방법으로부터 상당한 양의 실험오차를 가지고 있는 데이터로부터 의미 있는 깊이분포를 얻을 수 있었다. generalized cross-validation 방법을 이용하여 ARXPS 데이터로부터 regularization 방법에서 중요한 변수인 smoothing parameter 값의 최적치를 자동으로 구하도록 하였다.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is a sensitive, easily interpretable, and non-destructive technique for measuring the concentration of elements at the surface of materials. The XPS elemental composition represents an exponentially attenuated convolution of the actual composition depth profile of the sampled region. In angle-resolved XPS (ARXPS), spectra are collected as the photoelectron take-off angle from the sample is varied. Because the effective sampling depth increases with the increase of the sine of the take-off angle, it is possible to extract information on the concentration depth profile of the sample from ARXPS data. Spectra collected at each angle still contain a convolution of the entire depth profile, so the data must be inverted to generate an estimate of the depth profile[1-6]. The schematic diagram for ARXPS measurement is shown in Fig. 1.

Several numerical methods have been applied to utilize potentials of ARXPS technique[6]. Among those, regularization method has shown its applicability to more complex systems than simple

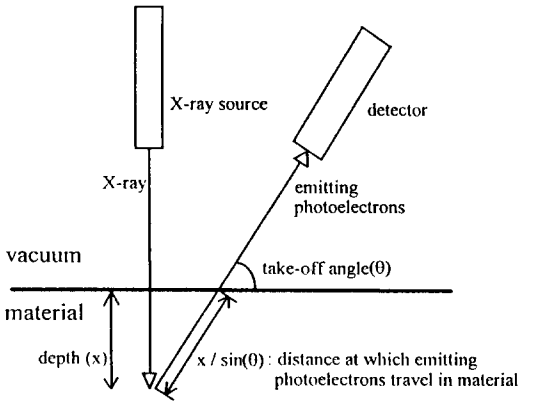


Fig. 1. Schematic diagram for ARXPS measurement.

overlay sample systems[1, 3]. In mathematics, various types of the regularization method have been investigated. However, results from mathematical studies have not been easily implemented into ARXPS data analysis mainly due to inherent physical constraints in the ARXPS experiment. This study compares two types of the regularization method (singular system and Hausdorff moment problem (HMP) approaches) which chemists have employed for ARXPS data analysis without fully understanding mathematical characteristics of the methods. Also, this simulation study investigates the effect of parameters used in the numerical method to recover the concentration depth profile from ARXPS data. The parameters which have considerable effect on the successful application of the numerical method include the number of data, sampling schemes, the choice of smoothing parameter, and errors on the data. The simulation study is essential because the major obstacle in obtaining concentration depth profiles from ARXPS data is located at the mathematical data treatment stage and there are no available standard samples with complex concentration depth profiles.

Measured intensity of the photoelectron flux at take-off angle of θ_n is given by Eq. 1.

$$F'(\theta_n) = K\int_0^\infty f(x') \exp\left(\frac{-x'}{\lambda \sin(\theta_n)}\right) dx' \qquad (1)$$

where $F'(\theta n)$ is the absolute signal intensity of an element in a sample, K is the normalization parameter, f(x') is the concentration depth profile of an element, x' is the depth from the surface, λ is the electron attenuation length, and θ_n is the angle between the sample surface and the photoelectron trajectory used in n-th measurement. With $x = x'/\lambda$ and $p_n = 1/\sin(\theta_n)$, the measured intensity of the photoelectron flux can be represented as Laplace transform of the concentration depth profiles (Eq. 2).

$$F(p_n) = \int_0^\infty f(x) \exp(-x\, p_n) dx \qquad (2)$$

The inversion of ARXPS data to get the concentration depth profile is one of mathematically notorious 'ill-posed' problems. If standard numerical inversion techniques are employed, the meaningful depth profiles cannot be generated[4-6].

Regularization method has been used to invert Laplace transform[3, 6, 7-10]. In the regularization method, inversion is carried out for a Fredholm integral equation of the second kind (Eq. 3) which has a stable and unique minimum for values of smoothing parameter which is not equal to zero.

$$\varphi(f(x)) = \| \int_0^\infty f(x) \exp(-x\, p_n)\, dx - F(p_n) \|^2 + \mu \| f(x) \|^2 \qquad (3)$$

where $\varphi(f(x))$ is a Fredholm integral equation of the second kind, μ is the smoothing parameter, and regularized solution, $f_\mu(x)$, is the solution which minimizes $\varphi(f(x))$. The smoothing parameter is introduced to reduce the unstability of the solution of Eq. 3 and provide an unique and meaningful solution.

Singular system approach[11-16] is one type of the regularization method. It uses conceptually similar mathematical treatment to singular value decomposition method widely used in the matrix inversion. The singular system of the Laplace

transform is defined by α_k, $\mathbf{u}_k$, and $\mathbf{v}_k$ where α_k is the k-th singular value, $\mathbf{u}_k$ is the k-th singular function, and $\mathbf{v}_k$ is the k-th singular vector. Using the singular system approach, the regularized solution is given by

$$f_\mu(x) = \sum_{k=1}^{N} \frac{\alpha_k}{(\alpha_k^2 + \mu)} \mathbf{u}_k \sum_{n=1}^{N} (F(p_n)\, \mathbf{v}_k(n)) \qquad (4)$$

where N is the number of the data. Here, the solution, $f_\mu(x)$, is represented as the linear combination of exp(-x p_n) functions because $\mathbf{u}_k$ is the linear combination of those functions. Since the solution is the linear combination of exponentially decreasing functions, it tends to approach to zero as the depth, x, increases to the infinity.

HMP approach[6, 17] converts Laplace transform integral to matrix form after substituting variable, x, with exp(-t).

$$F(p_j) = \int_0^1 f(-\ln(x)) t^{pj-1} dt$$

$$= \sum_{i=1}^{N} W_i\, t_i^{pj-1}\, f(-\ln(x_i)) \qquad (5)$$

The regularized solution for the HMP approach is

$$f_\mu(-\ln(x)) = \mathbf{A}^T F(p)\, (\mathbf{A}^T\mathbf{A} + \mu\, \mathbf{I})^{-1} \qquad (6)$$

where $\mathbf{A}$ is a matrix whose component, A_{ij}, is given by $(w_i\, t_i^{pj-1})$, $\mathbf{A}^T$ is a transpose of the $\mathbf{A}$ matrix, and w_i is the weight for Gaussian quadrature formula[18].

In the regularization method, major problem is that the smoothing parameter is an arbitrary parameter and criteria must be developed to select a smoothing parameter value which is large enough to stabilize the solution, and yet small enough so that real features are not smoothed out of the solution. Generalized cross validation (GCV) method proposed by Wahba[19-21] is based on the idea of letting the data themselves choose the value of the smoothing parameter. It is required that a good value of the smoothing parameter should allow the prediction of missing data values. No *a priori* information about the solution and/or the random error included in the data is required. In the GCV method, the optimal smoothing parameter value is obtained by minimizing GCV function, $V(\mu)$.

$$V(\mu) = N \,\|\, [\mathbf{I} - \mathbf{A}(\mu)]\, F(p) \,\|^2 \,/\, \|\, \mathrm{Tr}[\mathbf{I} - \mathbf{A}(\mu)] \,\|^2 \qquad (7)$$

where $\mathbf{A}(\mu) = \mathbf{A}\mathbf{A}^T(\mathbf{A}\mathbf{A}^T + \mu\mathbf{I})^{-1}$, $\mathrm{Tr}[\mathbf{I} - \mathbf{A}(\mu)]$ is the trace of the $[\mathbf{I} - \mathbf{A}(\mu)]$ matrix, N is the number of the data, and $\mathbf{I}$ is an identity matrix.

All the calculations were performed using IBM PC compatible 486 computer and it usually took a few minutes to get the solution from the simulated data. The program was written in C language using Microsoft QuickC for Windows compiler.

2. Results and Discussion

The application of numerical methods to obtain f(x) of Laplace transform using the data are dependent on several factors such as mathematical formulations, the number of the data, sampling scheme, and the error included in the data[14-16]. In the ARXPS measurement, such parameters are mainly bounded by the physical geometry of ARXPS instruments. Typical parameters are sampling angle range (θn = 90-15 degree; p_n = 1.0-3.8), effective sampling depth (up to 4λ), acceptance angle (5-15 degree) which limits the number of the data, and contained uncertainty (up to 10%) in the ARXPS data. In this study, the effect of such parameters was investigated.

Simulated data with random Gaussian errors, $F(p_n)$, were generated using several types of concentration depth profiles; $F(p_n) = F(p_n)'\ (1 + \sigma n)$ where $F(p_n)'$ is the generated data with zero random error and σn is Gaussian random error with specific relative standard deviation such as 1 and

10%. With the generated data, $F(p_n)$, the singular system and HMP approaches were used to recover an original concentration depth profile by solving the Fredholm integral equation of the second kind (Eq. 3). All the calculations were performed ten times for each case where ten different random values for a specific error were used to generate the data. The optimal value of the smoothing parameter was determined by the application of the GCV technique. To compare the results, relative error, L(%), of the recovered depth profile is used. The L(%) is the magnitude of the difference between the recovered and the original depth profiles divided by the magnitude of the original depth profile as shown in Eq. 8.

$$L(\%) = \| f_\mu(x) - f_o(x) \|^2 / \| f_o(x) \|^2 \times 100(\%) \quad (8)$$

The characteristics of the singular system and HMP approaches were evaluated for $f(x) = \exp(-x/2)$ case. In Fig. 2(a), representative f(x)'s obtained by the application of the singular system approach from the data with 1% and 10% errors are shown. Results for the data with 1% and 10% random errors demonstrate the utility of the method. It is clear that the method provides stable, consistent, and reasonable depth profiles with considering the error contained in the data. The GCV technique is imperative for the applicability of the method because it is important to find the value of the smoothing parameter which ensures the stable, consistent, and reasonable solution. For the GCV technique, the information on the uncertainty of the data is not required. Since the uncertainty of the real data is usually not known, the GCV technique is quite valuable.

The HMP approach provides qualitatively similar results for the data with 1% and 10% errors to those of the singular system as shown in Fig. 2(b). For the data with no error, the solution was obtained by the application of conventional inversion method. The solution appears unstable at the shallow region although the overall feature follows the original f(x). The conventional inversion in the singular system approach for the data with no error provides almost identical solution with the original f(x). The difference is due to the different mathematical formulations employed by the two approaches. It is well known the inverse of a matrix becomes more ill-posed as the size of the matrix increases. Results for the data with no error in Table I shows that the HMP approach produces much different solution from the original f(x) when the number of the data is eight. When the number of the data is six or four, the HMP approach shows little ill-posedness. Since the HMP approach employs the matrix manipulation, the larger number of the data can adversely affect the data analysis. On the contrary, the singular system approach produces the best result for the data with no error when the number of the data is eight. The solution of the singular system approach is the

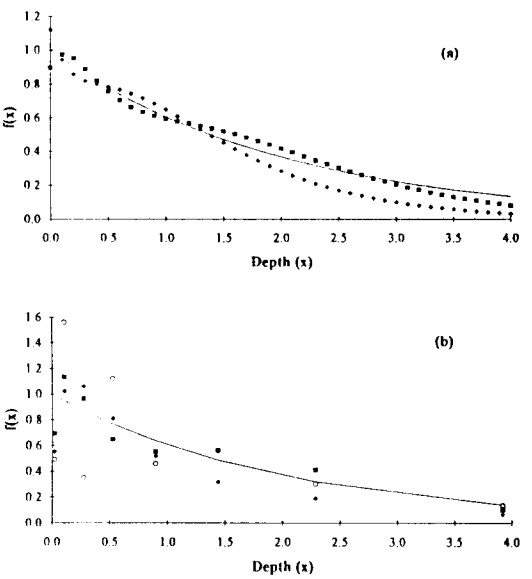


Fig. 2. Representative f(x)'s obtained by the application of (a) the singular system and (b) the HMP approaches from the data with 0% (o), 1% (■), and 10% (◆) errors. Original f(x) is shown as a solid line. Number of the data = 8.

linear combination of the exp(-p_nx) functions, where the number of the functions is that of the data. The solution with the larger number of the functions can better describe the original f(x).

By the application of the regularization technique, the unstability of the solution shown in the eight data case of the HMP approach is smoothed out and even the data with 1% and 10% errors produce the better results (Fig. 2(b) and Table I). The ill-posedness of the matrix still affects the results for the 1% and 10% error cases and the singular system approach performs better. However, the amount of the error included in the data is crucial. As the amount of the error increases, the discrepancy between the solution and the original f(x) increases.

Since it is known that the effect of sampling method is considered significant in the application of the regularization method[11-13], different sampling schemes such as equidistance, gravimetric, and equiangular samplings which can be employed in the ARXPS measurement are evaluated. In the equidistance sampling, the take-off angles (θ_n) during the measurements are set as $p_n = c + d$ (n-1) where $p_n = 1/\sin(\theta_n)$, c and d are parameters, n = 1, 2, ..., N, and N is the number of the data. When the number of the data is determined, the values of c and d are arranged to cover the range of the take-off angles (θ_n = 90-15 degree). In the gravimetric sampling, $p_n = c\ d^{n-1}$ and in the equiangular sampling, $\theta_n = c + d$ (n-1). As shown in Table II, the differences between the results of the different sampling schemes are not notable. The gravimetric sampling design was reported to provide better results than those from the equidistance sampling design[9, 13-15]. The studies emphasized that the range of the sampling points is important to be large and the value of the initial sampling point should be very close to zero. Since sampling points in the ARXPS measurement are in a limited range (p_n = 1.0-3.8) and the initial sampling point starts from 1.0, different sampling designs do not show significant differences.

Table 1. Relative error, L(%), of the solutions for the different number of the data.

	HMP approach			singular system approach		
random error on the data	number of the data					
	8	6	4	8	6	4
0 (%)	51.2	1.9	1.5	0.8	2.2	6.2
1 (%)	22.7	18.5	6.2	8.7	11.0	8.2
10 (%)	27.5	21.4	14.5	16.7	16.8	16.9

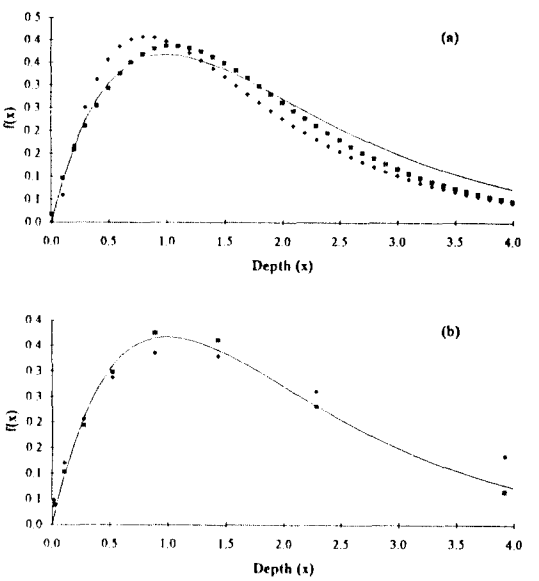
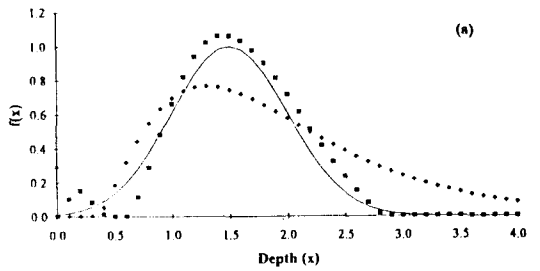


Fig. 3 Representative f(x)'s obtained by the application of (a) the singular system and (b) the HMP approaches from the data with 1% (■) and 10% (◆) errors. Original f(x) is shown as a solid line. Number of the data = 8 and f(x) = x exp(-x).

The regularization method were applied to other types of depth profile function such as f(x) = x∗exp(-x), exp(-2∗(x-1.5)^2), and a step function. For the f(x) = x∗exp(-x), representative solutions obtained by the application of the HMP and singular system approaches are shown in Fig. 3. Both approaches produce quite accurate solutions for the data with 1% error. For the data with 10% error, the two approaches produce less accurate solutions, and yet they are qualitatively reasonable ones with considering the amount of the error included in



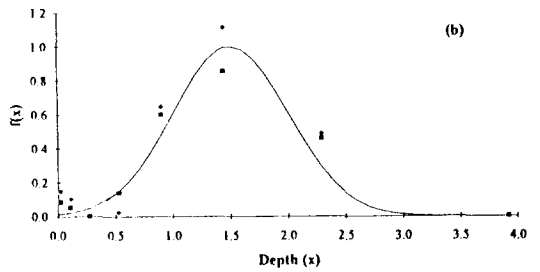
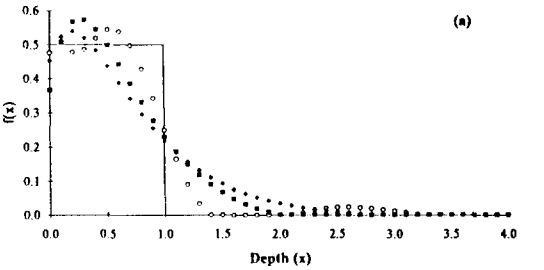


Fig. 4. Representative f(x)'s obtained by the application of (a) the singular system and (b) the HMP approaches from the data with 1% (■) and 10% (◆) errors. Original f(x) is shown as a solid line. Number of the data = 8 and $f(x) = \exp(-2*(x-1.5)^2)$.



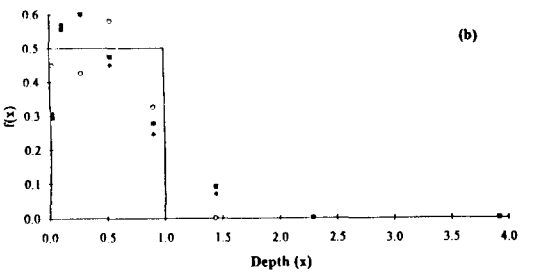


Fig. 5. Representative f(x)'s obtained by the application of (a) the singular system and (b) the HMP approaches from the data with 0% (o), 1% (■), and 10% (◆) errors. Original f(x) is shown as a solid line. Number of the data = 8 and f(x) is a step function.

the data. The results are very promising because the extraction of the depth profile information from the complex depth profile system is only feasible by the application of the regularization method. Furthermore, the regularization method demonstrates its applicability because the comparable results between two types of the approaches were obtained for the 1% and 10% error cases although two approaches employed the different mathematical formulations.

Representative solutions for the $f(x) = \exp(-2*(x-1.5)^2)$ are shown in Fig. 4. The stable and qualitatively accurate solutions are obtained for the data with 1% error. The singular system approach produces qualitatively different solution from the original f(x) for the data with 10% error. The HMP approach provides better solution. It is probable that the singular system approach would not well portray the function type of the $\exp(-x^2)$ because the regularized solution is the linear combination of the exp(-x) functions. If the results of the two approaches are comparable, it would be regarded as the obtained solutions are accurate. Since the standard ARXPS samples with the complex types of the depth profile are not available, the combinational use of two approaches would be quite valuable for confirming the validity of the results.

Table 2. Relative error, L(%), of the solutions for the different sampling schemes with $f(x) = \exp(-t/2)$ and the eight sampling data. (HMP and SS indicate HMP and singular system approaches, respectively)

random error on the data	equidistance sampling		gravimetric sampling		equiangular sampling	
	HMP	SS	HMP	SS	HMP	SS
1 (%)	22.7	8.7	22.3	8.2	24.7	9.4
10 (%)	27.5	16.7	28.1	19.7	30.1	15.1

For the step function type of the depth profile, two approaches produce smooth solutions as shown in Fig. 5. The step function resembles the simple overlay sample system most frequently investigated by the ARXPS technique. For the sample system, most valuable chemical information is the location of the interface which is not clearly determinable in the regularization method. The regularization method extracts the stable solution by introducing the smoothing parameter. The solution is inherently smooth which is contrary to the nature of the step function. The overlay sample can be analyzed by using the exact analytical solution for its Laplace transform without the inverse operation[1, 4, 5]. The method works well for the overlay sample. However, the extraction of the information on the depth profiles of the more complex sample systems are only possible using the regularization method.

3. Conclusions

Various types of concentration depth profile from the simulated data with considerable random error are obtained using two types of the regularization method. The singular system and the HMP approaches provide stable, consistent, and qualitatively accurate solutions for the complex depth profile systems with considering the large amount of errors on the data.

Optimal smoothing parameter values are obtained by the application of the GCV technique. With the GCV technique, the information on the uncertainty of the data is not required *a priori*. Since the uncertainty of the real data is usually not known, GCV technique is quite valuable.

The gravimetric sampling design was reported to provide better results than those from the equidistance sampling design. In that case, the initial sampling point is very close to zero. Since sampling points in ARXPS are in a limited range (p_n = 1.0-3.8), different sampling designs do not show much significant differences. The effect of the different sampling design becomes minor one due to the physical limitation imposed in the ARXPS measurement.

The regularization method produces different results according to the types of the depth profiles. The step function type of the depth profile is recovered as much smoothed form. The regularization method works well for the smooth depth profiles such as exp(-x/2), x*exp(-x), and exp(-x^2) functions. The applicability of the regularization method to such complex depth profiles is demonstrated in this study.

References

1. B.J. Tielsch and J.E. Fulghum, *Surf. Interface Anal.* **21**, 621(1994).
2. J.E. Fulghum, *Surf. Interface Anal.* **20**, 161(1993).
3. B.J. Tyler, D.G. Castner, and B.D. Ratner, *Surf. Interface Anal.* **14**, 443(1989).
4. T.D. Bussing and P.H. Holloway, *J. Vac. Sci. Technol.* **B6**, 1514(1988).
5. T.D. Bussing and P.H. Holloway, *J. Vac. Sci. Technol.* **A3**, 1973(1985).
6. P.C. McCaslin and V. Young, *Scanning Microsc.* **1**, 1545(1987).
7. P. Brianzi and M. Frontini, *Inverse Problems* **7**, 355(1991).
8. B. Davies and B. Martin, *J. Comput. Phys.* **33**, 1(1979).
9. J.P. Butler, J.A. Reeds, and S.V. Dawson, *SIAM J. Numer. Anal.* **18**, 381(1981).
10. J.M. Varah, *SIAM J. Numer. Anal.* **4**, 164(1983).
11. M. Bertero, C. De Mol, and E.R. Pike, *Inverse Problems* **1**, 301(1985).
12. M. Bertero, C. De Mol, and E.R. Pike, *Inverse Problems* **4**, 573(1988).
13. M. Bertero, P. Brianzi, and E.R. Pike, *Inverse Problems* **1**, 1(1985).
14. M. Bertero, P. Brianzi, and E.R. Pike, *Proc. R. Soc. Lond.* **A398**, 23(1985).
15. M. Bertero, P. Boccacci, and E.R. Pike, *Proc. R. Soc. Lond.* **A393**, 51(1984).
16. M. Bertero, P. Boccacci, and E.R. Pike, *Proc. R. Soc. Lond.* **A383**, 15(1982).

17. R. Bellman, R.E. Kalaba, and J.A. Lockett, *Numerical Inversion of the Laplace Transform* (Elsevier Publishing Company, INC., New York, USA, 1966).
18. W.H. Press, B.P. Flannery, S.A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in C* (Cambridge University Press, Cambridge, England, 1988).
19. G.H. Golub, M. Heath, and G. Wahba, *Technometrics* **21**, 215(1979).
20. P. Craven and G. Wahba, *Num. Math.* **31**, 377(1979).
21. G. Wahba, *SIAM J. Numer. Anal.* **140**, 651(1977).