



Estimating the Condition Number of a Matrix of Variables in Spectrochemistry. Case Study: Doublet and Triplet Structures

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Abstract: For the first time, it was shown theoretically that the condition number of the matrix representing individual bands of the multiplex structure of a spectrum profile is a power function of the band separation. This function strongly depends on the number of the structure components. The results obtained are confirmed by computer modelling. Possible practical applications are discussed.

Keywords: spectrochemistry; condition number; doublet and triplet spectrum structure; quantitative analysis errors.

I. Introduction

Mathematical methods of chemometrics, such as multivariate regression, discriminant analysis, and decomposition of complex spectral profiles [1], are widely used in spectrochemistry for data processing. The main tool of these methods is a matrix of variables, which consists of the spectra of the pure mixture components or the elementary spectral lines. The condition number of the matrix of variables is the means of estimating the accuracy of qualitative and quantitative results [2]-[4]. However, the condition number may be calculated only numerically [5], the theoretical estimation of this value for any arbitrary matrix being impossible. Therefore, it would be interesting to solve this problem in some particular simple cases, e.g., when the matrix columns are the components of spectral doublets and triplets. Such structures are important constituents of numerous spectral profiles. In this study, we establish the relationship between the condition number and the structure parameters, which allows preliminary evaluating this number without computer calculations. Standard notations of linear algebra are used throughout the paper. Bold upper-case and lower-case letters denote matrices and vectors, respectively. Upper-case and lower-case italicized letters denote scalars.

II. Gaussian Doublet

Suppose that the columns of matrix of variables $\mathbf{A} = [\mathbf{a}_1, \mathbf{a}_2]$ are equal-width (w) components of the Gaussian doublet which has its maxima at $\pm x_0$:

$$a_{qi} = r_q \exp(-(x_i \pm x_0)^2), \quad (1)$$

where $q = 1, 2$; $i = 1, 2, \dots, m$; r_q is the relative intensity of the component q ($r_1 + r_2 = 1$), $x_i = \beta i/w$, $x_0 = \beta i_0 w$, and $\beta = 2(\ln 2)^{1/2}$. From (1) it follows that

$$\mathbf{A}\mathbf{A}^T = \begin{bmatrix} r_1^2 \sum_{i=1}^m \exp(-2(x_i - x_0)^2) & r_1 r_2 \sum_{i=1}^m \exp(-2(x_i^2 - x_0^2)) \\ r_1 r_2 \sum_{i=1}^m \exp(-2(x_i^2 - x_0^2)) & r_2^2 \sum_{i=1}^m \exp(-2(x_i + x_0)^2) \end{bmatrix}. \quad (2)$$

If m is large enough, then the exponents sharply decay to zero and the sums in (2) can be replaced by integrals over infinite limits. These integrals can be calculated analytically as [6]

$$\mathbf{A}\mathbf{A}^T = Z \begin{bmatrix} R & p \\ p & 1/R \end{bmatrix}, \quad (3)$$

where $Z = r_1 r_2 (\pi/2)^{1/2}$, $R = r_1/r_2$, and $p = \exp(-2x_0^2)$.

The condition number of matrix $\mathbf{A}\mathbf{A}^T$ is

$$\text{cond}(\mathbf{A}\mathbf{A}^T) = \lambda_1/\lambda_2, \quad (4)$$

where λ is the eigenvalue of matrix $\mathbf{A}\mathbf{A}^T$ ($\lambda_1 \geq \lambda_2$). The eigenvalues are the solution of the following equation:

$$\det(\mathbf{A}\mathbf{A}^T - \lambda \mathbf{I}) = 0, \quad (5)$$

where $\det$ is the determinant symbol and $\mathbf{I}$ is the identical matrix. From (3)-(5) we obtain

$$\text{cond}(\mathbf{A}\mathbf{A}^T) = (1 + (1 - T)^{1/2})^2 / T, \quad (6)$$

where $T = 4(1 - p^2)/(R + 1/R)^2$. If $x_0 \ll 1$, then $T \ll 1$ and

$$\text{cond}(\mathbf{A}) = (\text{cond}(\mathbf{A}\mathbf{A}^T))^{1/2} \approx (R + 1/R)/2x_0. \quad (7)$$

The values of $\text{cond}(\mathbf{A})$ (7) calculated theoretically for x_0 up to 0.5 are very close to those obtained by computer modeling: e.g., 5.001, 2.021, and 1.15 for $x_0 = 0.2, 0.5$, and 1, respectively for $R = 1$. The corresponding theoretical values obtained from (7) are 5, 2, and 1.

III. Symmetrical Doublet

In the general case, we will describe the shape of a spectral line (band) by even function $F(x)$ which reaches its maximum at $x = 0$. Suppose that there exist derivatives $F(x)^{(t)}$, where $t = 1, 2, \dots$, and $n = 2l + 1$. Assume that $F(x \pm x_0)$ can be approximated by the Taylor series containing a finite number of terms:

$$a_{1i} = F(x_i - x_0) = \sum_{t=0}^n (-1)^t \frac{x_0^t}{t!} F_i^{(t)}, \quad a_{2i} = F(x_i + x_0) = \sum_{t=0}^n \frac{x_0^t}{t!} F_i^{(t)}, \quad (8)$$

where $i = -k, -k + 1, \dots, 0, k - 1, k$ and $F_i^{(t)}$ is the i -element of vector $\mathbf{F}^{(t)}$ (for the initial line, $t = 0$). Then,

$$\mathbf{A}\mathbf{A}^T = \begin{bmatrix} C_1 & D \\ D & C_2 \end{bmatrix}, \quad (9)$$

where

$$C_1 = \|\mathbf{a}_1\|_2^2 = \sum_{t=0}^n \frac{x_0^{2t}}{(t!)^2} \|\mathbf{F}^{(t)}\|_2^2 + 2 \sum_{p=0}^n \sum_{q>p}^n (-1)^{p+q} \frac{x_0^{p+q}}{p!q!} \sum_{i=-k}^k F_i^{(p)} F_i^{(q)}, \quad (10)$$

$$C_2 = \|\mathbf{a}_2\|_2^2 = \sum_{t=0}^n \frac{x_0^{2t}}{(t!)^2} \|\mathbf{F}^{(t)}\|_2^2 + 2 \sum_{p=0}^n \sum_{q>p}^n \frac{x_0^{p+q}}{p!q!} \sum_{i=-k}^k F_i^{(p)} F_i^{(q)}, \quad (11)$$

$$D = \sum_{i=1}^m a_{1i} a_{2i} = \sum_{t=0}^n (-1)^t \frac{x_0^{2t}}{(t!)^2} \|\mathbf{F}^{(t)}\|_2^2 + 2 \sum_{p=0}^n \sum_{q>p}^n (-1)^{p+q} \frac{x_0^{p+q}}{p!q!} \sum_{i=-k}^k F_i^{(p)} F_i^{(q)}, \quad (12)$$

where $\|\cdot\|_2$ is the symbol of Euclidean norm. Since $\sum_{i=-k}^k F_i^{(p)} F_i^{(q)} = 0$ when $p + q$ is an odd number,

$$C_1 = C_2 = C. \quad (13)$$

To eliminate zero members in the following expressions, we change the indexes of the corresponding sums and, from (4), (5) and (9)-(13), obtain:

$$\text{cond}(\mathbf{A}) = \left(\frac{C+D}{C-D} \right)^{1/2} = \frac{1}{x_0} \frac{\|\mathbf{F}^{(0)}\|_2}{\|\mathbf{F}^{(1)}\|_2} \left(\frac{1+Q(x_0)}{1+P(x_0)} \right)^{1/2}, \quad (14)$$

$$\text{where } Q(x_0) = \left(\sum_{t=1}^l \frac{x_0^{4t}}{(2t!)^2} \|\mathbf{F}^{(2t)}\|_2^2 + 2 \sum_{p=0}^{l+1} \sum_{\substack{r=1, \\ q=p+2r \leq n}}^l \frac{x_0^{p+q}}{p!q!} \sum_{i=-k}^k F_i^{(p)} F_i^{(q)} \right) / (\|\mathbf{F}^{(0)}\|_2^2),$$

$$P(x_0) = \left(\sum_{t=1}^l \frac{x_0^{4t+2}}{((2t+1)!)^2} \|\mathbf{F}^{(2t+1)}\|_2^2 \right) / (\|\mathbf{F}^{(1)}\|_2^2).$$

For $x_0 \leq 0.5$, polynomials $Q(x_0)$ and $P(x_0) \ll 1$. Under these conditions,

$$\text{cond}(\mathbf{A}) = \frac{1}{x_0} \frac{\|\mathbf{F}^{(0)}\|_2}{\|\mathbf{F}^{(1)}\|_2}. \quad (15)$$

It is easily to show that for $x = (-\infty, +\infty)$, $\|\mathbf{F}^{(0)}\|_2 / \|\mathbf{F}^{(1)}\|_2 = 1$ and $2^{1/2}$ for Gaussian and Lorentzian ($F(x) = \frac{1}{(1+x^2)^2}$; $\beta = 2$) curves, respectively (the ratio obtained for Gaussians is in accordance with (7) for $R = 1$). The same values of $\|\mathbf{F}^{(0)}\|_2 / \|\mathbf{F}^{(1)}\|_2$ are obtained for $x = (-w, +w)$. However, reducing this interval to the resolution limit $(x = (-x_0^{\text{lim}}, +x_0^{\text{lim}}))$, $x_0^{\text{lim Gauss}} = 0.424$, $x_0^{\text{lim Lorentz}} = 0.288$ [7] increases $\|\mathbf{F}^{(0)}\|_2 / \|\mathbf{F}^{(1)}\|_2$ to 1.43 and 1.95 for Gaussian and Lorentzian curves, respectively.

IV. Symmetrical Triplet

Suppose that a new spectral line $\mathbf{a}_3$ is positioned at the central point ($x = 0$) of the doublet (8):

$$a_{3i} = RF(x_i), \quad (16)$$

where R is the maximum line intensity. Then

$$\mathbf{A}\mathbf{A}^T = \begin{bmatrix} C & D & E \\ C & D & E \\ E & E & L \end{bmatrix}, \quad (17)$$

where $E = \sum_{i=-k}^k a_{1i} a_{3i} = R \sum_{t=0}^l \frac{x_0^{2t}}{(2t)!} \sum_{i=-k}^k F_i^{(0)} F_i^{(2t)}$, and $L = R^2 \|\mathbf{F}^{(0)}\|_2^2$.

With account for (17), equation (5) has the form:

$$(\lambda - M)[\lambda^2 - \lambda(M + E) + ML - 2E^2] = 0, \quad (18)$$

where $M = C + D$. Equation (18) has the following 3 roots, listed in descending order:

$$\begin{aligned} \lambda_1 &= [M + L + ((M - L)^2 + 8E^2)^{1/2}]/2 \\ \lambda_2 &= M \\ \lambda_3 &= [M + L - ((M - L)^2 + 8E^2)^{1/2}]/2. \end{aligned} \quad (19)$$

As a result, the condition number can be expressed as

$$\text{cond}(\mathbf{A}) = \frac{\lambda_1}{\lambda_3} = \frac{M+L + [(M-L)^2 + 8E^2]^{1/2}}{2(ML - 2E^2)^{1/2}} \approx \frac{2^{1/2}(2+R^2)\|\mathbf{F}^{(0)}\|_2^2}{Rx_0^2 [\|\mathbf{F}^{(0)}\|_2^2 \|\mathbf{F}^{(0)}\|_2^2 - (\sum_{i=1}^m F_i^{(0)} F_i^{(2)})^2]^{1/2}} \quad (20)$$

for $x_0 < 1$. The values of $\text{cond}(\mathbf{A})$ calculated theoretically according to (20) for x_0 up to 1 are very close to those obtained by computer modeling: e.g., 74.5, 11.7, and 3.05 for $x_0 = 0.2, 0.5$, and 1, respectively, in the case of Gaussians ($R = 1$). The corresponding theoretical values obtained from (20) are 75, 12, and 3.

V. Asymmetric Lines

In this section, we approximate the shape of a spectral line by asymmetric Gaussian [8] and Lorentzian [9] functions (Fig. 1):

$$F^{\text{Gauss}}(x_i - x_0) = \exp\left(-(x_i - x_0)^2 / (1 + \tau(x_i - x_0))^2\right), \quad (21)$$

$$F^{\text{Lorentz}}(x_i - x_0) = \exp\left(-\tau(1 - \tan^{-1}(x_i - x_0))\right) / (1 + (x_i - x_0)^2), \quad (22)$$

where τ is the line asymmetry parameter. For profile (22), two values of τ were used: 0.2 and 0.5. For profile (21), the corresponding values, - 0.0519 and - 0.1142, were calculated so as to provide the same asymmetry coefficient for Gaussian and Lorentzian lines:

$$\gamma = \mu_3 \mu_2^{3/2}, \quad (23)$$

where the n th central moment ($n \geq 2$) is: $\mu_n = \int_{-\infty}^{\infty} (i - \mu_1)^n F(i) di$, $\mu_1 = \int_{-\infty}^{\infty} i F(i) di / \int_{-\infty}^{\infty} F(i) di$.

Since the direct algebraic calculation of the condition number for functions (21) and (22) is very complicated, the numerical method was used. The results presented in Fig.2 clearly demonstrate linear dependences of the condition number on $1/x_0$ for doublets and on $1/x_0^2$ for triplets, in full agreement with equations (15) and (20), respectively. The impact of low asymmetry levels is negligible. This result is explained by the relatively small contribution of the asymmetric line wings to the condition number value.

VI. Discussion

Based on the above theoretical expressions, the following expression can be obtained if the separation parameter of the line maxima $x_0 < 1$:

$$\text{cond}(\mathbf{A}) = \Phi(R) x_0^{-(z-1)}, \quad (24)$$

where $\Phi(R)$ is the function of the relative component intensities and of the component spectral profiles (in particular cases (7) and (20) for $R \gg 1$ and $R \ll 1$, $\Phi(R) \sim R$ and $\sim 1/R$, respectively) and z is the multiplicity parameter. Statement (24) was confirmed by computer modeling of the quartets ($z = 4$): the sum of doublet (8) and $F(x_i - 2x_0) + F(x_i + 2x_0)$.

Figure 1 Spectral line profiles.

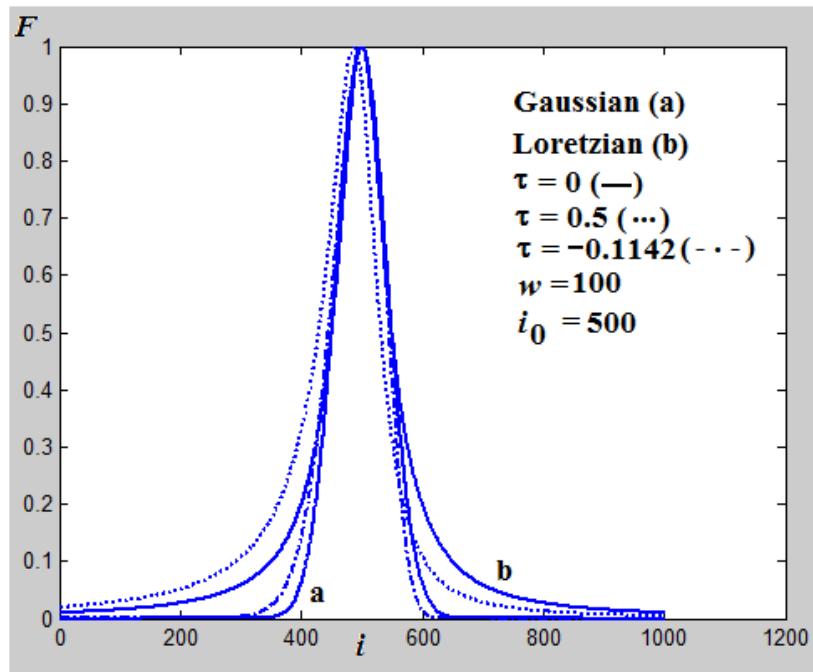
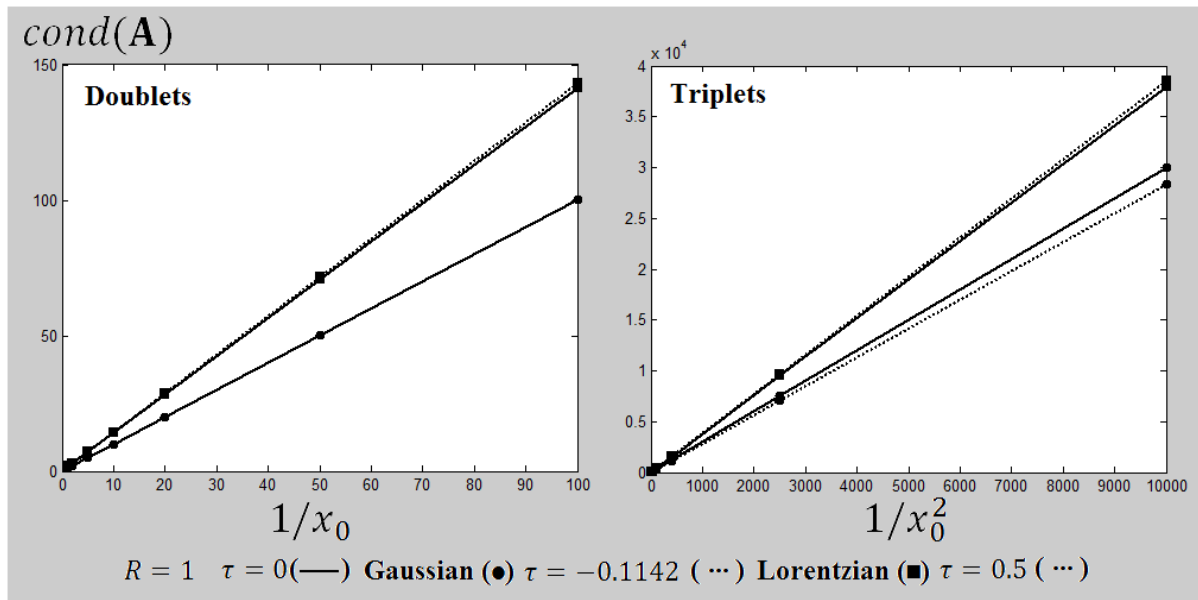


Figure 2 Impact of the line asymmetry on the condition number value.



It is known that the relative uncertainty of prediction in multivariate calibration [4] is

$$\frac{\|\delta x\|}{\|x\|} \leq \text{cond}(\mathbf{A}) \left(\frac{\|\delta \mathbf{A}\|}{\|\mathbf{A}\|} + \frac{\|\delta y\|}{\|y\|} \right), \quad (25)$$

where $\frac{\|\delta \mathbf{A}\|}{\|\mathbf{A}\|}$, $\frac{\|\delta y\|}{\|y\|}$ are the relative uncertainties of the modeling and the measurement errors, respectively. From (21) and (22) it follows that

$$\frac{\|\delta x\|}{\|x\|} \leq \Phi(R) x_0^{-(z-1)} \left(\frac{\|\delta \mathbf{A}\|}{\|\mathbf{A}\|} + \frac{\|\delta y\|}{\|y\|} \right). \quad (26)$$

Thus the prediction error is a power function of the pure-component line separation. This function strongly depends on the number of unresolved mixture component spectra ($x_0 \ll 1$). For example, the prediction error of the four-component mixture analysis by means of the Lorentzian quartet ($x_0^{\text{lim Lorentz}} = 0.288$) is more than ten times larger than the corresponding error for the two-component mixture analysis by means of the doublet if $R = \text{const}$. If the difference between the pure-component spectra intensities is very large ($\square \gg 1$ or $\square \ll 1$),

then $\square(\square)$ increases significantly and the prediction error (26) also increases. It can be concluded that it is the choice of well-resolved analytical lines of approximately equal intensity provides the minimum prediction error. However, in practice, such spectral features are very rare. The theoretical expressions obtained in this paper allow finding the compromise solutions in real-life situations.

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