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Computer Oriented Mathematical Models for Chemical System†

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The applications of computers to chemical problems are as wide and deep as chemistry itself. Advances in instrumentation, information science etc., resulted in chemometrics. Commonly occurring mathematical models applicable in various chemical problems are emphasized. Apart from direct solutions, application of iterative methods in solvent extraction equilibrium is given. Importance of simulated data and experimental optimization is indicated.

INTRODUCTION

Many of the developments of chemical analysis have followed closely on the heels of advances in electronics, statistics, computer science and engineering. Chemometrics[1–3] is an inter-disciplinary area which utilizes the concepts of advanced statistics and mathematics. Prior to 1960, statistics was employed without resort to computers but now it is impossible to ignore the effect of computer technology even on our lives.

In the past, chemical analysis utilised the newly discovered chemical phenomena. With recent advances in hyphenated techniques[4] a vast amount of chemical information is generated from which, unless properly processed, the fullest advantage cannot be derived. Further, in the present era fast data acquisition techniques[5,6], quick storage, timely retrieval and ultra-fast processing within reasonably short time without human prejudice are the bare minimum requirements for an analyst. Data processing is now in practice with micro-processors (*e.g.*, Intel 8085, 8086, 8088) mostly in a multiplexing mode. On-line processing of the data is more advantageous, as it saves time and human effort in transferring information acquired to a computer in a formatted form in an off-line mode.

Chemical Data Processing

Processing the data may range from simple number crunching to data reduction, optimization, dimension reduction, simulation, sensitivity analysis[7] etc. Computer Augmented Instruction, at various levels of education, in chemistry[8,9] and development of software for computer guided research ultimately leading to expert (knowledge based) systems are arousing wide interest among researchers now-a-days. The utility of

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some of these powerful mathematical and statistical techniques to a chemical problem is illustrated choosing a chemical model in solvent extraction. In this direction a computer program (EQCON)[10] is developed to process the data for a large number of samples for equilibrium study of a solute(s) in presence of a complexing agent (C) between water and an immiscible organic solvent. A complex (SC) is assumed to be formed in aqueous phase and the distribution of the solute between the two phases. The present version of the program calculates the equilibrium constant of the reaction $S + C \rightleftharpoons SC$ in aqueous phase which is a simple number crunching problem. Output consists of statistical parameters like standard deviation, student 't' limits etc.

The normality (or molarity) 'N' of a solution is calculated by weight of primary standard substance (W) in a specified amount of solvent (V). The extent of uncertainties in weight and volume dictated by the limitations in the instruments (balance and glassware) employed renders the understanding of errors on the final results more complex. The pessimistic errors in the concentrations of solutions either by weight method or by simple/multistage titrimetric technique are also outputted, which will help in the analysis of data by automatic curve fitting techniques or in optimizations.

Simulation of an Equilibrium in a Two Phase System

The art of mimicking the system is known as simulation[11-13] which requires the development of a mathematical model for the system and its solution by application of numerical technique.

The residual mass-balance equations for the distribution of I_2 between aqueous KI and an immiscible organic solvent are

$$I_2CAL - TI_2 = I_2(1 + D) + K^*KI^*I_2 - TI_2 \tag{1}$$

$$KICAL - TKI = KI + K^*KI^*I_2 - TKI \tag{2}$$

where TI_2 and TKI, I_2 and KI, and I_2CAL and KICAL are the total, equilibrium and calculated concentrations respectively. D is the distribution coefficient of iodine between water and organic solvent and K is the formation constant of the equilibrium, $KI + I_2 \rightleftharpoons KI_3$. Equations (1) and (2) can be written as

$$\begin{aligned} Z_1 &= X^*C1 + K^*Y^*X \\ Z_2 &= Y^*K^*Y^*X \end{aligned} \tag{3}$$

which are non-linear in X and Y and, of course, linear in parameters.

Solution of Over Determined Equations

In general, the equations, that one comes across in chemical research, are tabulated in Table 1.

TABLE 1

MATHEMATICAL MODELS APPLICABLE TO CHEMICAL PHENOMENA

$$Y_i = a_0 + a_1 * X_i \qquad (4)$$

$$Y_i = a_0 + a_1 * X_i + a_2 * ({}_{10}X_i) + a_3 * \log (X_i) * a_4 * X_i^2 \qquad (5)$$

$$Y_i = a_0 + a_1 * X_i + a_2 * X_i^2 + a_3 * X_i^3 \qquad (6)$$

$$Y_i = a_0 * (\exp\ (-a_1 * X_i)) \qquad (7)$$

$$Y = \frac{a_0 + a_1 * X_i + a_2 * X_i^2 + \ldots}{b_0 + b_1 * X_i + b_2 * X_i^2 + \ldots} \qquad (8)$$

Equation (4) is linear in parameters a_0 and a_1 and in explanatory variable X_i[14]. The linear dependence of absorbance on concentration and integrated form of first order kinetic rate equation are a few examples of linear equations. Equation (5) is linear in parameters (a_0, a_1, a_2 and a_3) but non-linear in variable (X_i)[15]. The concentration of mixed ligand complex is a non-linear function of equilibrium concentrations of metal ion and ligands while it is a linear function of the stability constants[16]. Equation (6) is a polynomial in variable and order of polynomial may range from 2 to K ($K > 2$). The dependence of enthalpy or e.m.f. on temperature follows a polynomial trend. Equation (7) is non-linear in parameter a_1 as well as variable X_i. The absolute rate constant of a reaction, elution times in chromatography follow this type of mathematical equations. Equation (8) is called rational function which is a quotient of two polynomials with the restriction $0 \leqslant X_i \leqslant 1$. Further if $b_0 = 1$, it is known as Pade approximation. Use of rational functions is made in interpreting excess parameters in mixtures of binary solvents.

The solution of non-linear equations[17] in variables is obtained by direct search methods. Gradient procedures and steepest descent technique. Direct search method was applied by Sillen in determining stability constant of metal complex in his Program LETAGROP[18]. Steepest decent method can be used to arrive at approximate solution of non-linear equations which when coupled with Marquardt logarithm[19] produces excellent convergent properties. Gauss-Newton and Newton-Raphson procedures are classified under gradient methods. Expansion of the non-linear equation by Taylor's infinite series and subsequent truncation after first degree terms produces Gauss-Newton formula while neglecting higher order terms than quadratic, results in Newton-Raphson technique.

Application of Gauss-Newton method to Eqs. (1) and (2) results in linear equations denoted by Eqs. (9) and (10).

$$[I_2(1 + D) + KI_3]*XI_2*XKI = I_2CAL - CI_2 \qquad (9)$$

$$[KI_3*XI_2] + KI + KI_3]*XKI = KICAL - CKI \qquad (10)$$

where XI_2 and XKI are fractional shifts.

In the matrix notation, Eqs. (9) and (10) are represented as

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} * \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \end{bmatrix} \tag{11}$$

and the solution vector X is obtained by

$$X = A^{-1} B \tag{12}$$

where A^{-1} is the inverse of A. However, in the simplest case consisting two equations, simple elimination procedure is adoptable. Since set of the linear equations are generated for non-linear equations (1) and (2), solution vector (12) represents only correction factor (shift) for the initial input (KI, I_2) parameters. The process of iteration—upgrading the previous values and repeating the same procedure until the difference between successive values is within the permissible limit, known as tolerance—is the basis of solving any system of non-linear equations.

Knowing the equilibrium concentrations of KI and I_2 under a given set of experimental conditions, the primary data, either volume of titrant or absorbance in spectrophotometric method, can be calculated. The data, thus obtained by varying various controllable parameters, is known as simulated data.

Sensitivity Analysis

The noise free data thus obtained throw light on the effect of simultaneous variation of influential controllable variables on the response parameter. Considering the system of present interest, the effect of errors in distribution constant, concentrations of various ingredients play an important role in the absorbance or volume of the titre.

The study of effect of errors of a single parameter in a multiparametric model forms the basis of sensitivity analysis. A parameter may be influential (a), non-influential (b) or alters the very trend (c) (Fig. 1). Simultaneous variation of two parameters produces simplex surfaces[20] which exhibit a

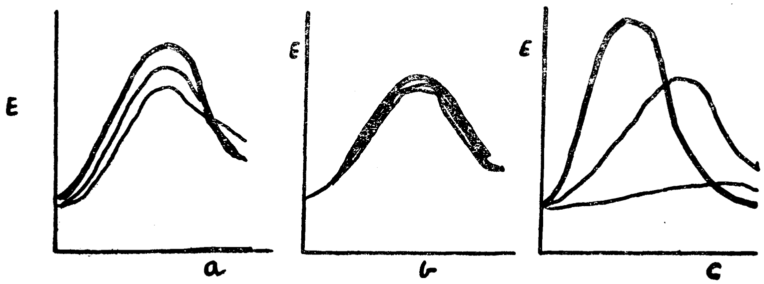

Fig. 1 Sensitivity Analysis of a Multiparametric model

maximum or minimum (Fig. 2). Maximization is to be adopted for extracting a solute, or absorbance of a coloured species, while minimization is needed while dealing with errors in different parameters. In either case the optimum conditions are obtained from simplex surfaces. For large number of parameters, optimum conditions are obtained only as a mathematical solution and computer is indispensable for solving such complex problems.

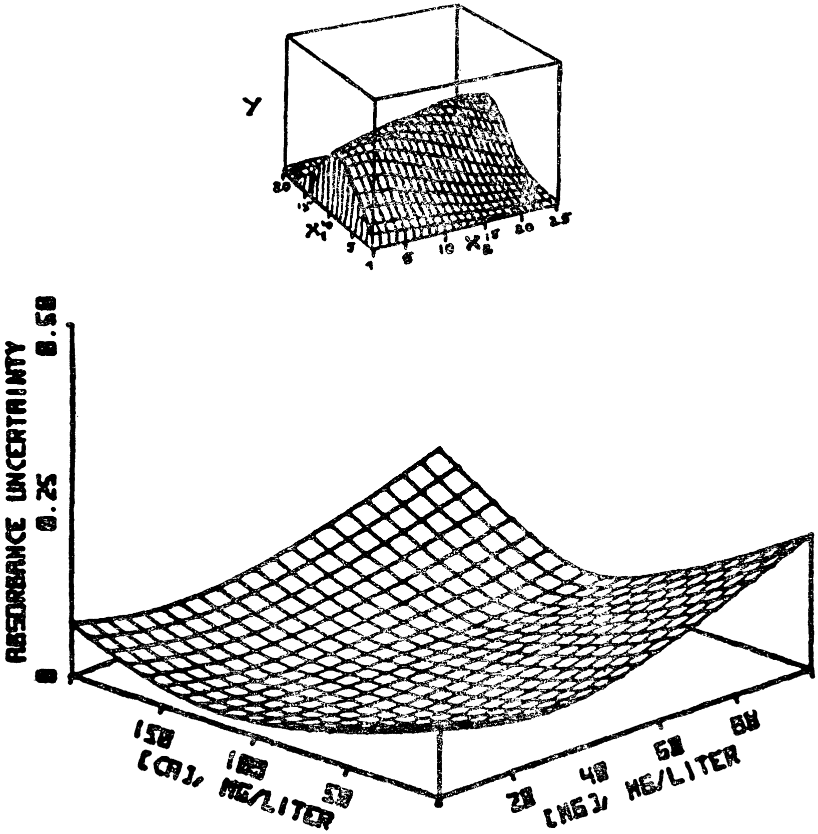

Fig. 2. Two-dimensional simplex figures: (a) Maximization and (b) Minimization of response.

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