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A PC COMPATIBLE COMPUTER PROGRAM FOR THE CALCULATION OF EQUILIBRIUM CONSTANTS BY THE SIMULTANEOUS PROCESSING OF DIFFERENT SETS OF EXPERIMENTAL RESULTS

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Summary—A new PC compatible computer program SIRKO for the calculation of the equilibrium constants by means of the simultaneous processing of different experimental data from various techniques is given. This program is characterized by the application of a universal response function, which allows many different physicochemical methods to be used to study equilibria without any modification of the program. It is also possible to refine additional parameters (electrode parameters, initial analytic concentration, *etc*). We have used the least-squares method with the weightings calculated according to the error propagation rule taking into account all independent variables. To minimize the function, singular Jacobian decomposition is applied. This allows control of its range and forms a set of parameters, determined from the experimental data.

Since the appearance of the early works of Sillen[1] dealing with algorithms for the calculation of equilibrium constants many different programs have been published.[2–8] Some papers[9–12] using this analysis show that these programs have varying potential uses, and that the various simplifications used in the majority of the programs allow processing of data for only one or few types of experiments (for example, SCOGS,[2] MINIQUAD,[3] TITFIT,[4] PROTAF[5]—potentiometric experiments; SQUAD,[6] LETAGROP-SPEFO[7]—spectrophotometric experiments).

Almost all these programs have been written for scientific computers (second or third generation computers) and these are not user friendly. Even when these programs have been translated for PC computers they are batch-oriented programs and the complete input desk must be prepared before the programs can be executed. Moreover, they do not use graphic presentation of data and thus do not carry a visual control for optimization.

However, as the authors[8] have noted, chemists need universal personal computer programs which are highly serviceable: that is, which do not need highly qualified operators and which allow the processing of a variety of physicochemical experiments. Here, the schemes used must be statistically rigorous: in particular, it is necessary to apply weighting factors calculated according to the error propagation rule, especially for simultaneous processing of data of different experimental types.

Hence, we have developed the program SIRKO for the calculation of equilibrium constants, and the refinement of additional parameters, from data obtained using different physicochemical methods. A distinctive feature of our approach is the use of the universal response function applicable to very many different experimental techniques. This allows analytical calculation of all necessary derivatives and weighting factors which increases the speed of our program. This also allows the inclusion of any independent variable into the set of refinable parameters, which eliminates systematic errors.

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To minimize the weighted summation of the squared deviation of calculated values from experimental ones, the method of the singular matrix decomposition of the first derivatives was used. This allows control of the matrix range and formation of a set of parameters which can be readily determined from a given series of experiments.

OPTIMIZATION PROCEDURE

A typical experiment for the study of an equilibrium process, for example, complexation, consists in the following: one group of the variables, called independent variables, is held constant, then another dependent variable is measured. Usually the volume of titrant added (V) is the independent variable, while the depended one is e.m.f. in potentiometry, or light absorption in spectrophotometric experiments.

In order to determine the relationship between the dependent and independent variables, it is necessary to construct a mathematical model of the equilibrium chemical system. The stability constants of the complexes form the parameters of this system. The parameters can be evaluated, for example, by the least-squares method, for which the best parameters are those which minimize the weighted summation of the squared deviations of the calculated values of the dependent variable from the measured ones:

$$U = \sum_i \sum_j W_{ij} \cdot (F_{ij}^{\text{exp}} - F_{ij}^{\text{calc}})^2, \qquad (1)$$

where i is the number of the series of experiments; j is the number of the experimental point in the given series; F_{ij} is the function of the parameters $Q_i (i = 1, \ldots, m)$, independent variables; $X_i (i = 1, \ldots, n)$ and V_{ij} below is called the response function;

$$F_{ij} = f_i(Q_1, \ldots, Q_m, X_1, \ldots, X_n, V_{ij}). \qquad (2)$$

The response function may have the same form for different series of experiments if the same physicochemical method is used for the study of the equilibria, or a different form, if several methods are used.

We will consider only one experiment, so that the formula will not be too cumbersome. Usually for the determination of the stability constants the Newton–Gauss method is used. Here, the function (1) is decomposed into Taylor's series, where only members of the first order are considered. Then, minimization of U gives a system of m equations relative to the correction on the initially preset parameters:

$$\tilde{\mathbf{J}} \cdot \mathbf{W} \cdot \mathbf{J} \cdot \Delta Q = \tilde{\mathbf{J}} \cdot \mathbf{W} \cdot \Delta F, \qquad (3)$$

where ΔF is the vector of deviation of the response function:

$$\Delta F_i = F_i^{\text{exp}} - F_i^{\text{calc}} \qquad (4)$$

and ΔQ the increment vector of the parameters:

$$\Delta Q_i = Q_i - Q_i^0,$$

W is the diagonal matrix of the weighting factors; **J** is the Jacobian matrix of the system with the elements:

$$J_{ij} = \frac{\partial F_i}{\partial Q_j}. \qquad (5)$$

The symbol ~ means the matrix transposition.

To solve the system of equations (3) the inversion of the matrix $\tilde{\mathbf{J}}\mathbf{W}\mathbf{J}$ is necessary, which is possible only when the determinant of the matrix differs from zero. If the determinant is not equal to zero, but is very small, then the matrix is considered poorly conditioned. Poor conditionality is expressed in the fact that the sum of the squares of deviations U alters within wide and unpredictable limits and does not converge to a minimal value. It often occurs when the selected initial values of the parameters are very far from those providing the minimum or if two or more parameters were highly correlated. Poor conditionality may be also due to insufficient experimental information. In these cases the problem of obtaining a stable solution of system (3) appears.

In our program, following Novikov and Rajevsky,[13] instead of the standard method based on the solution of the system of equations (3), the method of singular Jacobian decomposition is used. This method is the most reliable for solution of poorly conditioned systems of equation such as (3). It allows control of the range of the Jacobian matrix and forms a set of parameters which can be reliably determined from processed data.[14] For the singular decomposition the subprogram SVD[15] was used.

MATHEMATICAL MODEL OF THE EQUILIBRIUM CHEMICAL SYSTEM

To set the relationship between the dependent variable, independent variables and the parameters, it is necessary to design a mathematical model of the equilibrium chemical system. Here, it is convenient to use a formal-stoicheometric approach and to represent the reaction mixture as a stoicheometric matrix. Then, the transition from one model to another is readily realised by changing the stoicheometric matrix.

Using such an approach from S types of the particules C_i $(i = 1, \dots, S)$ the group of P independent components $B_j (j = 1, \dots, P)$ is selected and called the basis set. Any component C_i may be obtained from basis set via the relationship:

$$\sum_{j=1}^{P} \nu_{ij} \cdot B_j \overset{K_i}{\Leftrightarrow} C_i, \quad i = 1, \dots, S, \tag{6}$$

where ν is the stoicheometric matrix, of which the elements ν_{ij} represent stoicheometric coefficients of the component B_j in the i-th reaction. The reaction giving B_k is included in (6). That is, if C_i coincides with the component B_k of the basis, then $K_i = 1$ and $\nu_{ik} = 1$, while $\nu_{ij} = 0$ $(j \neq k)$.

At equilibrium, the following relationships are observed for the mass balance of the components

$$\sum_{i=1}^{S} \nu_{ij}[C_i] = b_j, \quad j = 1, \dots, P \tag{7}$$

and for the law of mass action

$$\ln[C_i] = \ln K_i + \sum_{j=1}^{P} \nu_{ij} \cdot \ln[B_j], \quad i = 1, \dots, S. \tag{8}$$

Here b_j is the total concentration of the component B_j the brackets designate the equilibrium concentrations of the corresponding components.

The calculation of the equilibrium concentration from these conditions may be carried out by different methods. The most convenient method which can be readily algorithmized is Brinkley's method.

The substitution of the equation (8) into (7) gives a system of P non-linear equations relative to P unknowns $\ln[B_l]$:

$$\sum_{i=1}^{S} \nu_{ij} \cdot \exp\left(\ln K_i + \sum_{l=1}^{P} \nu_{il} \cdot \ln[B_l]\right) = b_j,$$

$$j = 1, \dots, P. \tag{9}$$

The solution of this system is carried out by Newton's iteration method. The linearised system of equations has the form:

$$\mathbf{Z} \cdot \Delta = \Psi, \tag{10}$$

where $\mathbf{Z}$ is the symmetric Jacobi's matrix of the system of equations (9) with the elements:

$$\mathbf{Z}_{lj} = \sum_{i=1}^{S} \nu_{il} \cdot \nu_{ij} \cdot [C_i], \tag{11}$$

Ψ is the residual vector, the elements of which are:

$$\psi_j = b_j - \sum_{i=1}^{S} \nu_{ij} \cdot [C_i].$$

Δ is the vector of corrections to the initially pre-set values of $\ln[B]$.

$$\Delta_i = \ln[B_i] - \ln[B_i^0]. \tag{12}$$

Iterations are repeated until:

$$\Delta_i < \epsilon, \quad i = 1, \dots, P,$$

where ϵ is the specified accuracy of the solution.

It has been shown[17] that matrix $\mathbf{Z}$ is positive, and that the solution of system (9) is unique and will always converge from any initial approximation. However, if the majority of the summations in the Jacobi's matrix differs from any other by a factor less than the machine epsilon, then the matrix can become poorly conditioned due to the loss of accuracy, and the method fails.

Thus, the projection method proposed by Bugaevsky[16] is, to our mind, a more reliable method for the calculation of equilibrium concentrations. This method involves two-step iterations refining vector C_i. The first step transposes the initial vector $[C_i]$ into $[C_i']$ satisfying equation (7) according to the equation:

$$[C_i'] = [C_i] + \sum_{j=1}^{P} \nu_{ij} \times \left(\sum_{l=1}^{P} \mathbf{Z}_{jl}^{-1} \cdot \left(b_l - \sum_{k=1}^{S} \nu_{kl} \cdot [C_k]\right)\right). \tag{13}$$

The second projection transposes the concentrations obtained, $[C_i']$, into $[C_i'']$ satisfying equation (8) according to the equation:

$$\ln[C_i''] = \ln K_i + \sum_{j=1}^{P} \nu_{ij} \cdot \sum_{l=1}^{P} \mathbf{Z}_{jl}'^{-1} \times \left(\sum_{k=1}^{S} \nu_{kl} \cdot [C_k'] \cdot (\ln[C_k'] - \ln K_k)\right). \tag{14}$$

Here $\mathbf{Z}^{-1}$ and $\mathbf{Z}'^{-1}$ are the matrices which are inverse Jacobi's matrices for the system (9) at the concentrations $[C_i]$ and $[C_i']$, respectively.

The iterations are repeated until convergence is reached, which is decided by the summation of modulus of the relative increments of concentrations. We have used both Brinkley's method and the projection method. The solution of the linear system in Brinkley's method or matrix inversion in the projection method was carried out using triangular decomposition of the positively defined symmetrical matrix **Z** according to Choletsky's method.[15] The matrix **Z** is further used to determine the derivatives of the response function.

RESPONSE FUNCTION

To make the program universal, *i.e.* that it should allow processing of the results for different physicochemical methods and does not demand specialized knowledge, we use here the universal response function. This function is prescribed in an explicit form that differentiates our method from that proposed by others;[8] in MICMAC, for example, before starting, the user must define the response function in block MOSP. On using another type of experiment it must be changed. Moreover, all the derivatives in the program MICMAC are calculated by numerical methods which increases the calculation time. To use analytical derivatives these must be also given by a user for each type of experiment.

To avoid all these complications we use a universal response function describing the most widely physicochemical methods for investigation of equilibrium as follows:

$$F = Y_0 + Y_e \cdot \sum_{k=1}^{S} E_k \cdot [C_k] - Y_1 \times \lg\left(\sum_{k=1}^{S} EH_k \cdot [C_k]\right) \quad (15)$$

where F is the measured value; S the number of components in solution; $[C_k]$ the equilibrium concentration of the k-th component; Y_0 a constant value for a given method, often reflecting the solvent properties; Y_1 a scaling factor for potentiometric methods; Y_e a scaling factor additive methods; E_k the physicochemical parameter of the k-th component for additive methods; EH_k the parameter of the k-th component for potentiometric methods. A significant feature of our approach is the fact that all the parameters involved in response function (15), such as Y_0, Y_1, E_k, Eh_k, may act either as parameters or as independent variables.

The response function (15) allows analytical description of all the necessary derivatives for minimization of function (1). Thus, if Y_0, Y_1, E_k and EH_k act as parameters, then the corresponding elements of the matrix $\mathbf{J}_w$ may be easily determined from (15).

The derivatives with respect to the equilibrium constants (it is convenient to use $\lg K$ as the defined parameters) are also determined analytically as follows:

$$\frac{\partial F}{\partial \lg K_k} = \mathrm{f}\left(\frac{\partial [B_l]}{\partial \ln K_k}\right). \quad (16)$$

The derivatives $\partial[B_l]/\partial \ln K_k$ may be obtained taking into account the law of mass action as follows:

$$\mathbf{Z} \cdot X = D, \quad (17)$$

where **Z** is the same Jacobian matrix as for the calculation of the equilibrium composition with the elements calculated according to equation (11),

$$X_i = \frac{\partial B_i}{\partial \ln K_k}, \quad (18)$$

D is the vector of the free members determined as follows:

$$D_i = -\nu_{ki} \cdot [C_k]. \quad (19)$$

Besides refining the parameters Y_0, Y_1, E_k, EH_k it might also be necessary to refine the initial analytical reagent concentrations. The necessary derivatives can be also calculated in a similar manner as the derivatives with respect to the equilibrium constants. These newly calculated derivatives $\partial B_i/\partial \ln B_k$ are determined by a linear equation system similar to equation (17).

The principal suggestion, allowing use of the least-squares method, is that the errors in the measurement are random variables and subordinate the normal distribution law. In this case the errors of measurement σ_F are formed from the smaller errors σ_i, their dispersion being almost the same, while the distribution law for each of them is unrestricted. Thus, correct application of the least-squares method must use the weight factor which is calculated using the dispersions of both the observed value and the independent variable according to the law of error distribution. Hence, in our program we use the weight factors calculated as follows:

$$\frac{1}{W_i} = \sigma_{F_i}^2 + \sum_k \sigma_{X_k}^2 \cdot \left(\frac{\partial F_i}{\partial X_k}\right)^2, \quad (20)$$

where the summation extends to all the independent variables. The necessary derivatives $(\partial F_i/\partial X_k)$ are calculated analytically as at the formation of Jacobian $\mathbf{J}_w$. It should be noted that the weight factors calculated according to equation (20) will depend on the refined parameters, so they should be calculated for every iteration.

Thus, we obtain a statistically rigorous scheme of refinement of equilibrium constants and the additional parameters using the non-linear least-squares method.

PROGRAM SIRKO

On the basis of the described approach, we have worked out for the program a flow diagram which is given in Fig. 1. The program has been written in PASCAL for IBM PC and compatibles.

The subprogram 1 loads the data file created by subprogram 5. Using subprogram 2 it is possible to change the model of the equilibrium chemical system and the values of the parameters and independent variables. Subprogram 4 calculates from the covariation matrix **B**, the standard deviations and correlation coefficients of the determined parameters:

$$\mathbf{B} = (\mathbf{J}_w \cdot \mathbf{J}_w)^{-1} \cdot \frac{\sum_{i=1}^{L} (F_i^{\mathrm{exp}} - F_i^{\mathrm{calc}})^2}{(L - M)}, \quad (21)$$

where L is the number of experimental points and M is the number of determined parameters. This subprogram can also draw a diagram of the experimental and calculated titration curves as well as diagrams of the distribution of equilibrium concentrations.

Subprogram 3 optimizes parameters, and includes the following steps: (i) for each experimental point of every block (one series of the experiment is represented by a block) we calculate the equilibrium composition, the response function, weight factors and form a matrix $\mathbf{J}_w$. (ii) We find the singular decomposition of the obtained matrix. (iii) We check the convergence of function (1) using Hamilton's R-factor:

$$R = \sqrt{\left(\frac{U}{\sum_i W_i \cdot (F_i^{\mathrm{exp}})^2}\right)}. \quad (22)$$

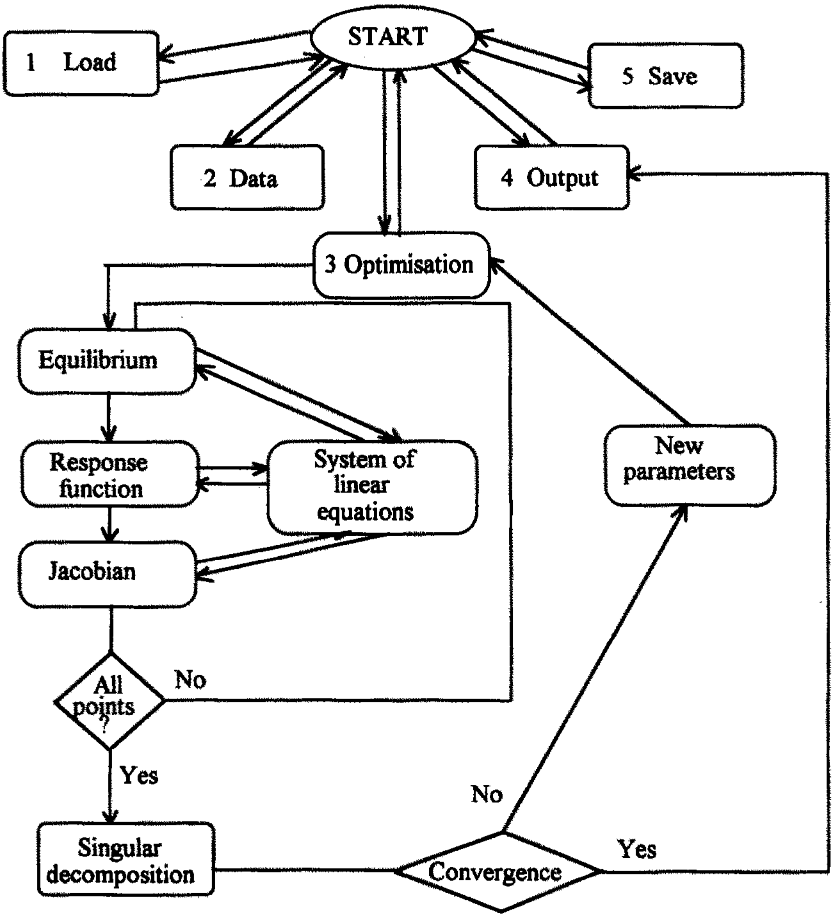

Fig. 1. Flow diagram of program SIRKO.

(iv) Then we terminate the iteration if $|R_i - R_{i-1}| < \epsilon$, where ϵ is the preset accuracy and i is the number of the iteration. Otherwise we calculate new values for the parameters and continue optimization. (v) To check the agreement of the chosen model with the experimental data, we compare the obtained values of the R-factor with the limiting value R_{lim}:

$$R_{\text{lim}} = \sqrt{\left(\frac{\sum_i W_i \cdot \sigma_i^2}{\sum_i W_i \cdot (F_i^{\text{exp}})^2}\right)},$$

where σ_i is calculated taking into account all the independent variables of the equation (20). The fit of the model with the experiment is considered satisfactory if $R < R_{\text{lim}}$. Otherwise, selection can be carried out according to Hamilton's criterion[19] which shows, at the preset L, M and level of significance, whether the difference between these two models is statistically significant. The response function used in our program describes well practically any type of experiment for measuring stability constants.

Thus, for spectrometry, having proposed $Y_1 = 0$ and all $EH_i = 0$, F will represent the optical density of the solution, E_i will reflect the molar indices of absorption, Y_e the thickness of the cells and Y_0 the optical density of the solvent.

In calorimetric experiments, F is the quantity of heat released or absorbed during the reaction, Y_e the volume and E_i the molar enthalpy of the complex formation.

For potentiometric experiments, having defined $Y_e = 0$ and $E_i = 0$, and $EH_i = \alpha_i$ (where α_i is the activity coefficient of the ion for which a reversible selective electrode is used) we obtain the ordinary Nernst equation. Here F may repreent either the potential in millivolts, in which case $Y_1 = \beta S$ and Y_0 is the zero potential, or in $PC_i = -\lg[C_i]$ for which $Y_1 = \beta$ and $Y_0 = 0$, where β characterizes the deviation of the electrode function from the theoretical Nernst equation. It is, thus, possible to take into account the effect of an interfering cation j, if EH_j is the selectivity coefficient.

In addition, this function may describe the behaviour of the electrode for pH measurement where it is often necessary to take into account junction potentials:[18]

$$\text{pH}_{\text{meas}} = \text{pH}_0 - \lg(\alpha \cdot [\text{H}]) + A \cdot [\text{H}] + B \cdot [\text{OH}]. \quad (23)$$

In this case, for equation (15), F should be considered as the measured values of pH, $Y_0 = \text{pH}_0$, where $EH \neq 0$ only for the proton for which $EH = \alpha$ and $E \neq 0$ for the proton ($E = A$) and for the hydroxyl ion ($E = B$).

Thus the chosen response function is universal and may be used for any type of experiment. It is convenient when the simultaneous processing of data from different experiments is carried out.

The significant characteristic of our approach is that the variables involved in equation (15) (such as Y_0, Y_1, E_k, EH_k) may act both as model parameters and independent variables. This is defined by the user. For example, when we are calibrating an electrode for which we do not know the junction potential, then EH_i and E_i should be considered as parameters and refined. In any subsequent work with this electrode, they may already be considered as independent variables. Similarly for spectrophotometry, if from a single experiment one can determine the molar absorption of a ligand, then E_i for the ligand can be defined as a parameter while in other experiments this value would be used as an independent variable.

It is rather simple for the user to change a parameter variable into an independent variable. Each parameter is defined with the key IP which can adopt the values 0, 1, 2. If $IP = 0$, then the corresponding value will not be refined, and thus it acts as an independent variable, its dispersion contributing to the weight factor according to the formula (20). If $IP = 1$ or 2 then the corresponding value is defined to be a parameter and will be refined. Moreover, if $IP = 1$, it is refined only in one block. If $IP = 2$, then this parameter is common for some blocks. Thus, if we determine the electrode parameters from a series of titration curves, and in some series the alkali concentration is not known, then both alkali concentration and electrode characteristics are model parameters. However, the electrode parameters will be common for the series of titration curves, while the alkali concentration will be common only for the corresponding titration curve.

The refinement of additional parameters helps to eliminate systematic errors, but here, as correctly noted in Ref. 5, they should be treated with caution, because this could lead to physically insignificant models, and so the refined parameters should be carefully scrutinised. In any case, if some additional parameters correlate strongly with other ones, then their value should be refined experimentally and subsequently used as an independent variable.

The application of the method of singular decomposition allows the analysis of the matrix J_w for conditionality. If matrix $\mathbf{J}_w$ is poorly conditioned, then at least one of the singular numbers σ_i will be considerably smaller than the others. If it corresponds to one of the additional parameters, then this parameter should be transposed into an independent variable, so as to improve the conditionality of the matrix $\mathbf{J}_w$, which leads to the non-uniqueness of the solution. If this is impossible, then such singular numbers should be assumed to be zero, giving a tendency to stability of the system solution (3). In practise these operations are equivalent to keeping constant weak parameters which cannot be reliably determined from the given experiment. According to a recommendation,[14] we have assumed zero such σ_i for which $\sigma_i/\sigma_{\max} < M\epsilon$, where ϵ reflects the relative accuracy of the initial data. For every singular number the set of zero components is listed. Any multiple μ of these coefficients may be added to the obtained solution of the system (3) without changing the residual vector by more than $\mu M\epsilon$. Thus the application of the singular decomposition represents valuable information on the reliability and sensitivity of the determined parameters.

CONCLUSION

In conclusion, the new program SIRKO presents the following set of advantages with respect to the already existing programs: (i) it uses an algorithm of singular Jacobian decomposition for non-linear parameters estimation. (ii) It is based upon a universal response function. (iii) It uses statistically a rigorous weighting scheme, which takes into account all independent variables. (iv) It is a menu-oriented system, with a friendly user interface. (v) It provides optional modules such as: the analysis of the rank of the matrix of absorbance of several solutions with different compositions, at several wavelength. The knowledge of this rank, which is equal to the minimum number of absorbing species in the solution studied, provides an objective criterion for the further interpretation of the spectrophotometric data. The analysis of potentiometric data according to Bjerrum, in order to calculate the average number $\bar{p}$ of protons fixed to a ligand, and average number $\bar{n}$ of ligands fixed to a coordination center. This program has now been used for the calculation of the complexation constants for macrocyclic compounds with metal cations from spectrophotometric data and from pH-metric titration.[21]

We have used SIRKO together with program MINIQUAD[3] and SUPERQUAD[22] PC versions, in the treatment of our direct and competition potentiometric experiments (H^+ or Ag^+ as auxiliary cations), and together with program LETAGROP-SPEFO[7] working on an IBM 6081 computer, in the treatment of our multi-wavelength spectrophotometric studies of the metallic complexation by the lower rim functionalized calixarenes.[23] In all cases, we concluded to an excellent agreement between the results given by SIRKO and the 'elder' programs. SIRKO has also been successfully compared to a standard program for the titration calorimetric study of the complexation of alkali and alkaline-earth cations by a series of *p*-*t*-butycalix[4]arene tetraamides.[24] The polyvalence of SIRKO, usable for any of the three types of experiments, and its interactivity, make SIRKO the best of all the programs we have used for our calixarene studies.

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