Talanta, Vol. 23, pp. 15–25. Pergamon Press, 1976. Printed in Great Britain

MULTIPARAMETRIC CURVE FITTING—I

COMPUTER-ASSISTED EVALUATION OF CHELATOMETRIC TITRATIONS WITH METALLOCHROMIC INDICATORS

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(*Received* 16 *September* 1974. *Revised* 22 *January* 1975. *Accepted* 16 *February* 1975)

Summary—A curve-fitting procedure has been developed for the photometric complex-formation titration of the metal–indicator complex MIn_N which is assumed to predominate in solution. By means of a least-squares procedure the following five parameters were determined: the end-point, the absorbance of the indicator complex A_{MIn_N}, the indicator concentration c_{In}, the stability constants and, if possible, K_{MY}. A modified version of Sillén's Letagrop Vrid has been used for the mathematical-statistical approach of the non-linear model based upon the non-transformed function $A = f(v)$. Additional information is obtained about the goodness of fit, indicating whether the chosen model with predominance of MIn_N is correct or not. The use of the program is demonstrated by application to chelatometric microtitrations of zinc and lead with EDTA, using Naphthylazoxine 6S and SNAZOXS as metallochromic indicators.

A number of authors[1–7] have been engaged in solving the problem of determination of the equivalence point, finding a suitable formulation of the fundamental equations or seeking optimum conditions for sharp end-point indication in photometric chelatometric titrations.

The theory of photometric titration with use of metallochromic indicators has been outlined in several basic contributions[1–3,6–17] Fortuin *et al.*[1] derived a general equation of the type $a = f(\alpha)$ where a is the titration parameter and $\alpha = [In']/c_{In}$, for the case where a single metal–indicator complex of 1:1 stoichiometry is formed. The theoretical discussion of the effect of various parameters on the shape of titration curves was illustrated by plots of families of curves calculated for different values of parameters K_{MIn}, K_{MY}, c_{In} and c_M. Ringbom and Wänninen[8] applied conclusions from the theory of photometric titrations using acid-base indicators, and pointed out the usefulness of pM for characterizing the system of a chelatometric titration. The pertinent equilibria were also solved in theoretical discussions[2,3] of visual end-point detection with metallochromic indicators in an attempt to characterize the sharpness of the indicator colour change. In both contributions the formation of a single MIn complex was considered and the plots of $\alpha = f(a)$ for various values of the parameters involved were also given. Kotrlý developed the theory of photometric titrations for a case where the indicator forms a predominating complex MIn_N (*cf.* ref. 6) or a stepwise equilibrium system of three indicator complexes[7] MIn_{N-2}, MIn_{N-1}, MIn_N. For a discussion of various effects on the shape of the titration curve he also used the transformation function $a = f(\alpha)$.

Several authors[9–17] have shown that M_2In_2 also occurs in solution and that large systematic deviations may occur when titrations are performed with very dilute solutions. For simplicity, graphical extrapolation of the linear parts of the titration curve close to the equivalence point is commonly used to locate the end-point. A computer program for this type of end-point evaluation can be conveniently based on the application of a simple linear regression (*e.g.*, see refs. 18, 19).

In some theoretical papers it is supposed that the equivalence point is known and that the parameter functions $a = f(\alpha)$ or $\alpha = f(a)$ can be studied. However, this condition is fulfilled only rarely in practical cases, and the evaluation of the end-point is sometimes complicated and accessible only by means of a graphical extrapolation.

An exception to graphical extrapolation is the approach by Sato and Momoki,[20] suggesting transformation of variables $g(1 - \alpha)/\alpha = f(v)$ and using graphical linearization without the stability constants K_{MIn} and K_{MY} being known beforehand. Corrections are made for volume change and indicator concentration and the paper appears to be, especially in practical cases, a most useful contribution.

A number of papers[4,8,21,22] use calculations of conditional stability constants, side-reaction coefficients, or their graphical interpretation, to explain the course

of the chelatometric titration curve. In all the papers the indicator concentration c_{In} is supposed to be known. Chemical analyses using paper and thin-layer chromatography have revealed, however, that chelatometric indicators are substances that often contain considerable amounts of impurities from raw materials, synthesis by-products and various isomers. The removal of such impurities is difficult and sometimes impossible because of decomposition of the dye. In some cases the indicator is the only species of the mixture which reacts with the metal being titrated. A correction for indicator purity has not been taken into account in the calculations in any of these papers.

Early attempts at computation of parameters from titration curves, including chelatometry, are described in the book by Dyrssen *et al.*[23] and are based on an application of Ringbom's method.[21] Sato and Momoki[24] selected an entirely different approach to the computer evaluation of a chelatometric titration curve involving the MIn chelate. They determined three unknown parameters: the end-point, the conditional stability constant $K_{MIn,cond}$, and $K_{MY,cond}$, with a least-squares fitting method using Deming's subroutine for the minimization process. The algorithm was demonstrated for the titration of magnesium with EDTA, Calmagite being used as indicator.

The change of absorbance during a chelatometric titration involving a metallochromic indicator forming a 1:1 complex was calculated by means of a computer.[25] In addition to the absorbance, the transmittance, the free metal-ion and indicator concentrations, and the stability constants of the metal–titrant and the indicator–metal complexes were calculated.

The present paper presents a new algorithm for the evaluation of a chelatometric titration curve when the MIn_N complex predominates, and determination of the following parameters: the end-point, pIn, log K_{MIn_N} and (if possible) log K_{MY}, and the absorbance of the indicator complex A_{MIn_N}. Additional information about the goodness of fit indicates whether this model is correct or not. The least-squares method for the minimization process is based on a modified version of Sillén's Letagrop Vrid.[26] The statistical treatment is quite different from that suggested by Sato and Momoki,[24] the fundamental equation being based on Kotrlý's approach[6] but regression analysis is applied to the function $A = f(v)$. The algorithm has been applied to the titration of zinc and lead, using Naphthylazoxine 6S and SNAZOXS as metallochromic indicators.

THEORETICAL

Equation of the photometric titration curve

End-point indication in a chelatometric titration using a metallochromic indicator is based on the displacement reaction between the indicator complex MIn_N and the chelate-forming ion of a titrant Y, which can be expressed by the overall equation

$$MIn_N + Y \rightleftharpoons MY + N\,In \qquad (1)$$

The equilibrium in equation (1), as written, presupposes that the metallochromic indicator forms only one complex, MIn_N. This complex has a colour different from that of the free form In, which may represent, however, a mixture of several differently protonated indicator species. The equilibrium is considerably affected by the hydrogen-ion activity, as this controls the concentration of the active forms of both competing ligands Y and In.

The chelatometric titration is usually carried out in a buffered solution. If the free indicator is predominantly in only one protonated form, *e.g.*, H_jIn, at a selected pH value, the absorbance of the titrated solution at a chosen wavelength, for a particular consumption of titrant v, is given by the equation

$$A = d\{\epsilon_{1N}[MIn_N] + \epsilon_{j1}[H_jIn]\} \qquad (2)$$

where d is the path-length of the cuvette, and ϵ_{1N} and ϵ_{j1} are the molar absorptivities of the species MIn_N and H_jIn, respectively. The dependence of the absorbance A on consumption of titrant v is represented by the photometric titration curve.

As the total concentration of indicator c_{In} is

$$c_{In} = [H_jIn] + N[MIn_N] = c_{In}\alpha + N[MIn_N] \qquad (3)$$

where $\alpha = [H_jIn]/c_{In}$ is the fraction of indicator in the free form, equation (2) can be transcribed as a function of this relative variable:

$$A = dc_{In}\cdot\frac{\epsilon_{1N}}{N} - dc_{In}\left\{\frac{\epsilon_{1N}}{N} - \epsilon_{j1}\right\}\alpha$$

$$= A_{(MIn_N)} - \{A_{(MIn_N)} - A_{(In)}\}\alpha \qquad (4)$$

As indicated in equation (4), the colour transition of an indicator is defined by the limiting values of the absorbance, for a point $\alpha = 0$, *i.e.*, $A_{(MIn_N)}$, where all the indicator is bound in the metal complex MIn_N, and for a point $\alpha = 1$ where the metallochromic indicator is completely converted into the free form In, *i.e.*, $A_{(In)}$.

If v ml of titrant are added to the original volume V_0 ml of titrand, the measured absorbance A_{exp} should be corrected for the dilution by means of the factor $g = V/V_0$, where $V = V_0 + v$:

$$A = A_{exp}g = A_{exp}\left\{1 + \frac{v}{V_0}\right\} \qquad (5)$$

To determine the theoretical value of the absorbance A from equation (4) for individual values of the titrant consumption v it is assumed that for the given set of conditional stability constants, *i.e.*,

$$K_{MIn_N,cond} = \frac{[MIn'_N]}{[M'][In']^N} \qquad (6)$$

$$K_{MY,cond} = \frac{[MY']}{[M'][Y']} \qquad (7)$$

where conditional concentrations are expressed by Ringbom's notation with respect to [M′], [In′], [MIn'_N], [Y′], [MY′], and for given total concentrations

$$c_Y = ac_M = [Y'] + [MY'] \quad (8)$$

$$c_M = [M'] + [MY'] + [MIn'_N] \quad (9)$$

$$c_{In} = [In'] + N[MIn'_N] \quad (10)$$

it is then possible to calculate the values of the relative variable α for each value of v. A general explicit expression of $\alpha = f(v)$ as a function of individual parameters is not possible, as it represents a real, positive root of a polynomial in α of degree $(2N + 1)$. Many authors prefer to express the inverse functions $v = f(\alpha)$ and $a = f(\alpha)$, where a is the equivalent fraction of titrant consumed:

$$a = \frac{vf_Y}{Vc_M} \quad (11)$$

f_Y being the molarity of the titrant. For a given equilibrium system the titration-curve equation can be derived in the form of transformed variables[6] as follows

$$a = 1 - \frac{c_{In}(1-\alpha)}{Nc_M}\left[1 + \frac{1}{K_{MIn_N,cond} \cdot c_{In}^N \cdot \alpha^N}\right] - \frac{1}{K_{MY,cond}\, c_M} + \frac{K_{MIn_N,cond} \cdot c_{In}^{N-1}}{K_{MY,cond}}\left[\frac{N \cdot \alpha^N}{1-\alpha} - \frac{c_{In} \cdot \alpha^N}{c_M}\right] \quad (12)$$

The values of the conditional stability constants $K_{MIn_N,cond}$ and $K_{MY,cond}$ necessary for insertion into equation (12) can be calculated from the corresponding stabiiity constants, provided that detailed information on all side-reactions is available. The side-reaction coefficients α_M, $\alpha_{Y(H)}$, *etc.*, give a true picture of all competitive effects. The definitions of these coefficients,[4,21] their dependence upon experimental conditions and the method of calculation (*cf.* ref. 22) are clarified in the literature quoted.

Regression analysis

When analysing experimental photometric titration curves it should be considered that in general the values of the following parameters are known either not at all or only approximately: the titrant consumption at the end-point, v_{ep}, the indicator concentration c_{In}, the initial limiting value of the absorbance A_{MIn_N}, and the values of the stability constants K_{MIn_N} and K_{MY}. These five parameters have to be determined by numerical analysis of the titration curve.

The equation of the chelatometric titration curve is formulated as a function $a = f(\alpha)$, *i.e.*, in terms of transformed relative variables and as an inversion function with respect to the original set of variables $(v; A)$. Considering that the reading of the volume on a microburette has a smaller error than the reading of the absorbance A, it is convenient for the application of a least-squares fitting method to take the volume v as an independent variable and absorbance A as a dependent variable. However, an explicit formulation of the absorbance from the equation of a chelatometric titration curve is not possible, as a polynomial function of degree $(2N + 1)$ would be obtained and an approximation method would be needed to find the particular real root of physical meaning. Therefore all previous authors usually worked with the inversion function $v = f(\alpha)$.

In applying the method of least-squares in order to determine the five unknown parameters of a chelatometric titration curve the assumption that the original error distribution of dependent variable A_{exp} is retained and that the original non-transformed function $A = f(v)$ can be used, should be fulfilled. An attempt was made to solve the problem by means of an indirect expression of a residuum ΔA when formulating the optimization criterion.[27] A more rigorous method is to use an approximation method, *e.g.*, the Newton iterative method.

In formulating the non-linear model it seemed convenient to make a formal rearrangement of equation (12) to give (13) for the ith point on the titration curve:

$$v_i = R\frac{\alpha_i^N}{1-\alpha_i} - S.\alpha_i^N - T\frac{1-\alpha_i}{\alpha_i^N} + Q.\alpha_i + W \quad (13)$$

where

$$R = \frac{K_{MIn_N,cond} \cdot c_{In}^{N-1} \cdot N \cdot v_{eq}}{KG_{MY,cond}} \quad (14)$$

$$S = \frac{K_{MIn_N,cond} \cdot V \cdot c_{In}^N}{K_{MY,cond} \cdot f_Y} \quad (15)$$

$$T = \frac{1}{K_{MIn_N,cond} \cdot N \cdot c_{In}^{N-1} \cdot f_Y} \quad (16)$$

$$Q = \frac{c_{In} \cdot V}{N \cdot f_Y} \quad (17)$$

$$W = v_{eq} - \frac{V}{f_Y}\left[\frac{c_{In}}{N} + \frac{1}{K_{MY,cond}}\right] \quad (18)$$

The chelatometric titration curve involves all the parameters to be determined in the expressions R, S, T, Q and W and so it is advantageous to investigate the contributions of these particular expressions to the shape of a titration curve. The members R, S, T, Q and W are useful for illustration how a change in the individual parameters can cause a change in the function U.

According to the optimization criterion the function U is given by

$$U = \sum_i w_i(A_i - A_{i,cal})^2 = \sum_i w_i(\Delta A_i)^2 \quad (19)$$

where w_i is the statistical weight, usually taken as unity. Absorbance A_{cal} is calculated from the equation

$$f(v, A) - v = \phi(A) \quad (20)$$

and the modified Newton iterative method

$$A^{(k+1)} = A^{(k)} - \eta \cdot \frac{\phi(A^{(k)})}{\phi'(A^{(k)})} \quad (21)$$

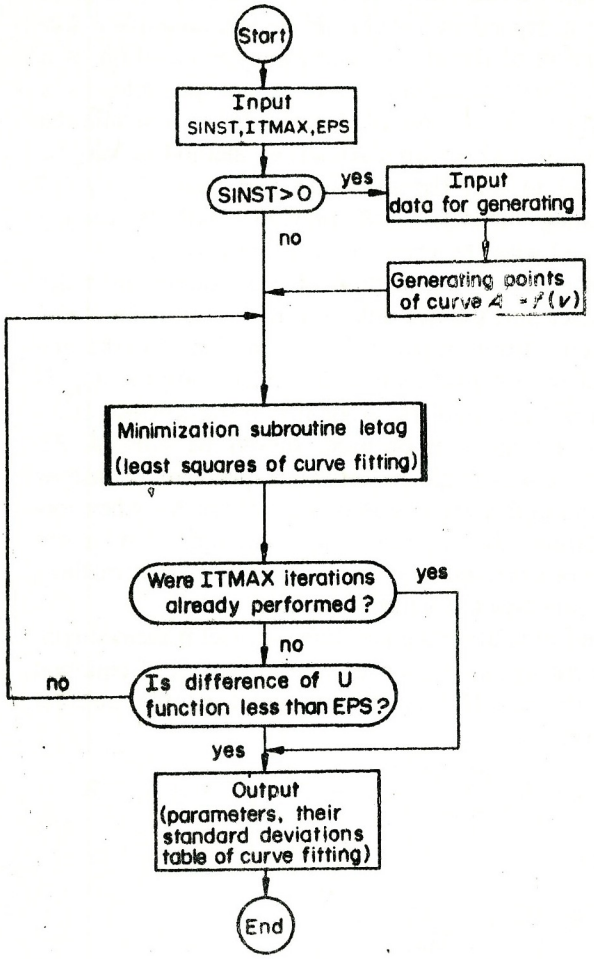

Fig. 1. Schematic flow chart of the program NCHEL-LETAG.

where η is a convergence coefficient, and ϕ' is the first derivative of ϕ. For the initial approximation the experimental value A_{exp} is used for $A^{(0)}$ in the iterative process.

COMPUTER PROGRAM

The schematic flow-chart of the program NCHEL-LETAG is given in Fig. 1. The program is written in Fortran and has been run on a Hewlett-Packard 2116 C computer, and is available on request.

NCHEL-LETAG consists of a main program which reads in a title and the part of the input needed for a simulation of titration curve points, if requested. It then calls subroutines as follows and organizes outputs of determined parameters, a table of curve fittings and a graph of curve fitting.

LETAG—this routine, which is Sillén's Letagrop Vrid adapted for a smaller computer and modified to the subroutine form,[28] performs the main minimization. The functional diagram of LETAG is given in Fig. 2. The subroutine contains "blocks" which are logical units; one of them, KNUT, is a switchboard to which the computer returns after fulfilling each task. Depending on which value for the control number Rurik it then reads, the computer jumps from KNUT to another block for a new task. The block DATA reads input data being called by Rurik 6. PUTS, a special block, follows the block DATA automatically (marked by a letter A) and may use these data to calculate some quantities which will be needed for further calculations. UBBE, called by subroutine LETAG or by the main program, calculates the error-square sum-function U defined by relationship (19). Block LASK, called by Rurik 7, reads in preliminary values for the parameters to be determined. STEG, called by Rurik 3 or 4, reads the general orders for systematic variation of parameters. (IK) means which parameter is to be varied, and by how much (W). LETA, called by Rurik 5, governs the systematic variation of the unknown parameters. Other blocks such as SKRIK or MIKO, PROVA, VRID, *etc.* are contained in the REST OF SUBROUTINE LETAG and their function is explained in another contribution[28] of this series.

RNDNR—a standard routine for the generation of errors having a normal Gaussian distribution—was adapted from Communications of the Association for Computing Machinery, Algorithm 314 (1968).

DATA—data input; some experimental constants describing titration condition are read in, then the calculation of side-reaction coefficients α_{M1n_N} and α_{MY}, follows and finally the matrix of titration data (v, A) or (v, T) is read in. The absorbance values are corrected for dilution and with regard to the reference solution. Titration curve points which are not contained in the interval (α_{min}, α_{max}) are then eliminated.

UBBE—this routine calculates A_{cal} for each volume v and a given set of parameters by the Newton iterative method. Then follows calculation of the error-square sum-function U.

Data input instructions

Simulated or experimental input data can be evaluated by the NCHEL-LETAG program. For a given set of parameters the absorbance ASIM, loaded by a calculated ERROR, is calculated for each volume v. Then a least-squares fit is applied to a set of (v; ASIM) and parameters XK(1), ..., XK(5) are evaluated. Such input data are illustrated in Table 1a. (*a*) 1 card: SINST is optional and is the instrumental error of the measured absorbance; when experimental data are to be evaluated then SINST < 0 and the other data on this card are not read; EPS1 is the absolute criterion of convergence of A_{cal} in the Newton iterative process; if $(A_{cal}^{(n)} - A_{cal}^{(n-1)}) <$ EPS1 then the iteration process terminates; EP2 is the η coefficient of convergence in the Newton iterative method; NX is the

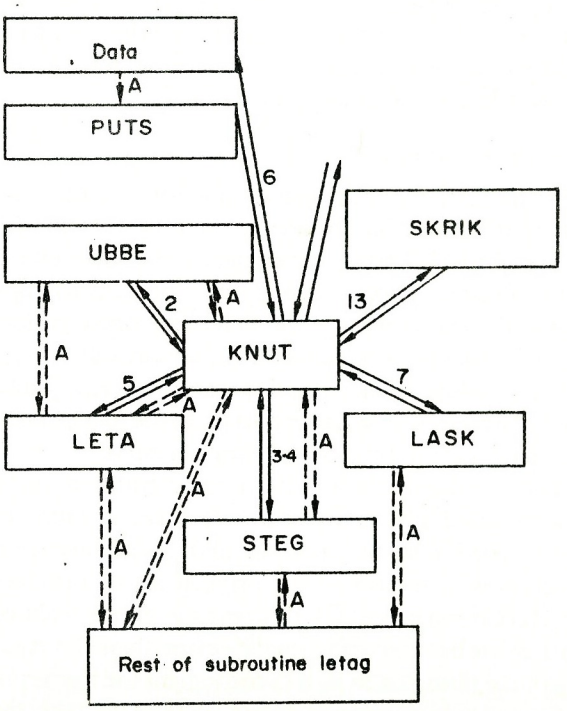

Fig. 2. Function diagram of minimization subroutine Letag.

Table 1*a*. Input data in case of previous simulation of titration curve are contained in principal parts A, B, C, and D

Data	Explanation
Part A	
0·001 0·008 0·9 5 0·31388	SINST EPS1 EP2 NX XK(1)
12·209 18·2 4·9314 0·17 2368	XK(2) XK(3) XK(4) XK(5) IR
Part B	
2 20 0·001 207·19 0·05 0·95 0	N VO FY VM ALMIN ALMAX ASB
0·53 5·75 27 0·171	AI PH NB X5
7·0 2·868 −3·0 −3·0	A(1) A(2) A(3) A(4) for ind.
10·26 6·16 2·67 2·0	A(1) A(2) A(3) A(4) for t.a.
0·1050 0·2575 0·1200 0·2621 0·1350 0·2675	VA(1) VA(2)...
0·1500 0·2730 0·1650 0·2805 0·1800 0·2896	
0·1900 0·2967 0·2000 0·3048 0·2100 0·3137	
0·2200 0·3249 0·2300 0·3378 0·2400 0·3527	
0·2500 0·3698 0·2550 0·3791 0·2600 0·3890	
0·2650 0·3989 0·2700 0·4099 0·2750 0·4214	
0·2800 0·4332 0·2850 0·4454 0·2900 0·4580	
0·2950 0·4709 0·3000 0·4840 0·3050 0·4974	
0·3100 0·5051 0·3150 0·5120 0·3500 0·5200	...VA(NB-1) VA(NB)
Part C	
0·00000001 30 1 6 6 0·9	EPS ITMAX NGR XL YL UF
("V in millilitres")	NAZX
("Absorbance")	NAZY
PB-SNAZOXS-EDTA system, 12. 11. 1973	Name of system
Part D	
7	RURIK CALL LASK
5 5	NK NBYK
0·31 12·0 18·2 5·0 0·165	XK(1) XK(2) XK(3) XK(4) XK(5)
1 1 1 1	ISKIN I J S(I, J)
3	RURIK CALL STEG
2	N
1 0·003	IK W
2 0·2	IK W
5	RURIK CALL LETA ↑
3	RURIK CALL STEG |
4	N |
1 0·001	IK W | one iteration
2 0·06	IK W |
4 0·03	IK W |
5 0·001	IK W |
5	RURIK CALL LETA ↓
3	
4	
1 0·003	
2 0·008	
4 0·006	
5 0·0008	

continued

5		3	3	*etc.*
3		4	4	
4		1 0·0001	1 0·00003	
1 0·0002		2 0·0015	2 0·00075	
2 0·004		4 0·002	4 0·001	
4 0·0035		5 0·00025	5 0·0001	
5 0·0005		5	5	
5		3	3	
3		4	4	
3		1 0·00006	1 0·00001	
1 0·00015		2 0·001	2 0·0005	
2 0·002		4 0·0015	4 0·0005	
4 0·00035		5 0·0002	5 0·00005	
5		5	5	

Table 1*b*. Output of program NCHEL-LETAG for simulated data from Table 1*a*

PB-SNAZOXS-EDTA system, 12.11.1973
Simulation for parameters

SINST	VEQ	LKMIN	LKMY	PCIN	AMIN
0·00100	0·31388	12·209	18·200	4·931	0·1700

Condition of titration

N	VO	FY	AW	ALMIN	ALMAX	PH	AI
2	20·0	0·00100	207·190	0·050	0·950	5·750	0·5300

INDICATOR:	PK11	PK21	PK31	PK41	ALPH(IN)(IN(H))(H)
	7·000	2·868	−3·000	−3·000	0·188E + 02
TIT. AGENT	PK11	PK21	PK31	PH41	ALPH(Y)(Y(H))(H)
	10·260	6·160	2·670	2·000	0·1156E + 06

Titration curve

	Experimental		Simulated	
V(ML)	AEXP	ALPHA	ASIM	ERROR
0·1050	0·2575	0·2494	0·2569	−0·0006
0·1200	0·2621	0·2630	0·2629	0·0008
0·1350	0·2675	0·2784	0·2682	0·0007
0·1500	0·2730	0·2944	0·2721	−0·0009
0·1650	0·2805	0·3157	0·2809	0·0004
0·1800	0·2896	0·3418	0·2915	0·0019
0·1900	0·2967	0·3620	0·2971	0·0004
0·2000	0·3048	0·3852	0·3060	0·0012
0·2100	0·3137	0·4105	0·3160	0·0023
0·2200	0·3249	0·4422	0·3245	−0·0004
0·2300	0·3378	0·4788	0·3386	0·0008
0·2400	0·3527	0·5210	0·3528	0·0001
0·2500	0·3698	0·5693	0·3684	−0·0014
0·2550	0·3791	0·5957	0·3797	0·0006
0·2600	0·3890	0·6237	0·3892	0·0002
0·2650	0·3989	0·6518	0·3970	−0·0019
0·2700	0·4099	0·6828	0·4087	−0·0012
0·2750	0·4214	0·7153	0·4216	0·0002
0·2800	0·4332	0·7488	0·4340	0·0008
0·2850	0·4454	0·7834	0·4449	−0·0005
0·2900	0·4580	0·8192	0·4605	0·0025
0·2950	0·4709	0·8556	0·4705	−0·0004
0·3000	0·4840	0·8928	0·4836	−0·0004
0·3050	0·4974	0·9308	0·4992	0·0018
0·3100	0·5051	0·9522		
0·3150	0·5120	0·9727		
0·3500	0·5200	0·9975		

Total number of points: 27 Number of points used: 24

Minimization process LETAG

I = 0	0·31000	12·0000	18·2000	5·0000	0·1650
I = 1 MINUSGROP U = 0·13454E − 03	0·31125	12·1523	18·2000	5·0000	0·1650
I = 2 MINUSGROP U = 0·68026E − 04	0·31225	12·1523	18·2000	4·9700	0·1650
I = 3 SIGY = 0·8783E − 02 U = 0·47436E − 04	0·31231	12·1603	18·2000	4·9640	0·1650
I = 4 SIGY = 0·1138E − 02 U = 0·23582E − 04	0·31308	12·1743	18·2000	4·9470	0·1649
I = 5 SIGY = 0·1054E − 02 U = 0·23305E − 04	0·31308	12·1726	18·2000	4·9470	0·1649
I = 6 SIGY = 0·1076E − 02 U = 0·22890E − 04	0·31314	12·1710	18·2000	4·9444	0·1644
I = 7 SIGY = 0·1033E − 02 U = 0·22591E − 04	0·31320	12·1683	18·2000	4·9436	0·1642
I = 8 SIGY = 0·1028E − 02 U = 0·22533E − 04	0·31323	12·1668	18·2000	4·9432	0·1641
.. .. ..		..	..	..	..
.. .. ..		..	..	..	..
I = 30 SIGY = 0·1045E − 02 U = 0·21869E − 04	0·31306	12·1327	18·2000	4·9469	0·1593

After 30 declared iterations at U value = 0·21869E − 04 and parameters:

VEQ = 0·31306 ± 0·00032
LKMIN = 12·1327 ± 0·0285
LKMY = 18·2000
PCIN = 4·9469 ± 0·0065
AMIN = 0·1593 ± 0·0041

Table 1*b*—*continued*

Calculated auxiliary values:
Milligrams of metal: 0·64862E − 01
Molar concentration of metal: 0·157E − 04
Molar concentration of indicator: 0·113E − 04

Table of curve fitting

V(ML)	A	ACAL	DEL A	DEL A KV	ALPHA
0·1050	0·2569	0·2571	−0·0002	0·6157E − 07	0·2669
0·1200	0·2629	0·2619	0·0010	0·9594E − 06	0·2838
0·1350	0·2670	0·2672	−0·0002	0·3688E − 07	0·2954
0·1500	0·2721	0·2734	−0·0013	0·1584E − 05	0·3098
0·1650	0·2809	0·2810	−0·0001	0·1775E − 07	0·3342
0·1800	0·2915	0·2901	0·0014	0·1875E − 05	0·3637
0·1900	0·2958	0·2969	−0·0012	0·1332E − 05	0·3757
0·2000	0·3050	0·3051	−0·0001	0·1962E − 07	0·4013
0·2100	0·3160	0·3146	0·0014	0·1877E − 05	0·4317
0·2200	0·3245	0·3252	−0·0008	0·5951E − 06	0·4552
0·2300	0·3386	0·3380	0·0006	0·4144E − 06	0·4942
0·2400	0·3528	0·3525	0·0003	0·1061E − 06	0·5334
0·2500	0·3676	0·3690	−0·0014	0·2034E − 05	0·5742
0·2550	0·3790	0·3784	0·0006	0·3051E − 06	0·6057
0·2600	0·3886	0·3882	0·0004	0·1603E − 06	0·6322
0·2650	0·3970	0·3984	−0·0013	0·1791E − 05	0·6555
0·2700	0·4087	0·4094	−0·0007	0·4793E − 06	0·6876
0·2750	0·4216	0·4210	0·0006	0·3924E − 06	0·7232
0·2800	0·4340	0·4330	0·0010	0·9845E − 06	0·7573
0·2850	0·4449	0·4452	−0·0003	0·8974E − 07	0·7877
0·2900	0·4605	0·4584	0·0021	0·4556E − 05	0·8305
0·2950	0·4705	0·4713	−0·0008	0·5790E − 06	0·8583
0·3000	0·4836	0·4848	−0·0012	0·1510E − 05	0·8944
0·3050	0·4992	0·4989	0·0003	0·1092E − 06	0·9376

number of parameters to be read in for generation of simulated error; XK(1) is the value of the first parameter, *i.e.*, equivalence point v_{eq}, in ml; XK(2) is the value of the second parameter, *i.e.*, the concentration stability constant of the indicator complex, log K_{MIn_N}; XK(3) is the value of the third parameter, *i.e.*, the concentration stability constant of complex with the titration agent, log K_{MY}; XK(4) is the value of the fourth parameter, *i.e.*, the total indicator concentration ($-\log c_{In}$); IR is the initial value for subroutine RNDNR and is the optional value from an interval (5; 6000), this interval is given by the word-length of the computer used and the algorithm RNDNR.

(*b*) 1 card: N is the stoichiometric coefficient in the indicator complex MIn_N; VO is the initial volume of solution to be titrated, in ml; FY is the molar concentration of the titrant; VM is the atomic weight of the metal to be titrated; ALMIN is the lower limit α_{min}; ALMAX is the upper limit α_{max}; ASB is the correction to be made to the sample absorbance for the absorbance of the reference solution.

(*c*) 1 card: AI is the absorbance of the free indicator measured after the titration is completed; PH is the pH value of the solution to be titrated; NB is the total number of points on the titration curve; X5 is the absorbance of the indicator complex measured before the titration A_{MIn_N}.

(*d*) 1 card: A(1), ..., A(4) are the four dissociation constants of the indicator acid; "−3" is written in place of any dissociation constant not available.

(*e*) 1 card: A(1), ..., A(4) are the four dissociation constants of the titrant; "−3" is written in place of any dissociation constant not available.

(*f*) A number of NB/5 cards: these contain the coordinates of experimental points on the titration curve: VA(I) is the volume v of titrant added; VA(I + 1) is the absorbance or transmittance value, depending on the switch 6.

(*g*) 1 card: EPS is the absolute criterion of convergence of function U; when $U^{(m)} <$ EPS then the minimization process is terminated; ITMAX is the number of iterations in the minimization process; NGR is the number which controls the plotter output; when it is not equal to zero then a graph is printed; data for the plotter are given by XL for the length of the abscissa and YL for the length of the ordinate (in inches); UF is a fraction specifying the change in the iterative steps for all parameters after each iteration.

(*h*) 1 card: NAZX, the description of the abscissa.

(*i*) 1 card: NAZY, the description of the ordinate.

(*j*) 1 card: descriptive title.

(*k*) 1 card: 7, Rurik, which calls block LASK to read the initial estimation of the parameters to be determined.

(*l*) 1 card: NK is the total number of parameters to be determined in the course of the LETAG minimization process; NBYK is the number of non-negative parameters to be determined.

(*m*) 1 card: XK(1), ..., XK(5), the initial guesses for the parameters to be determined.

(*n*) 1 card: ISKIN is the number of matrix elements to be read in; I or J denotes the co-ordinates of a matrix element; S(I, J) is the value of a matrix element.

(*o*) 1 card: 3, Rurik, which calls the block STEG where the minimization steps for each parameter are read in.

(*p*) 1 card: N is the number of parameters to be varied in an actual shot.

(*q*) 1 card: IK is the number of parameters for which the steps are read in; W is the value of a step; the pair (IK, W) is written for each varied parameter.

(*r*) 1 card: 5, Rurik, which calls the block LETA where a systematic variation of parameters is performed.

When the experimental titration curve is to be analysed, in part A, SINST is written equal to −1 and the values of parameters XK(1), ..., XK(5) are not written. Then follows part C, which calls block DATA, part B and part D.

Interpretation of output

At the top of the table, the name of the titration system, the parameters for a simulation process and the titration

conditions are printed together with the values of SINST, the five parameters, N, VO, FY, AW, ALMIN, ALMAX, PH, AI, and the pK_a values for the successive deprotonation of the indicator and the titrant, respectively, which are denoted as PK11, PK21, PK31, PK41. The proton side-reaction coefficients of the indicator and titrant are also printed as ALPHA IN(H) and ALPHA Y(H).

Experimental and simulated values are given in the following sequence: the volume of titration agent V(ML), the absorbance AEXP, the corresponding value of α, ALPHA, and last the simulated values of absorbance ASIM and calculated error ERROR if the simulation process is requested. Under the table the total number of experimental points is printed and the number of points within the interval α_{min}, α_{max} which are selected for regression analysis.

The outputs of the successive minimization processes can be controlled by switches and some parts of them can be omitted. The particular iterations are printed next and for each of them the standard deviation SIGY, the *U*-function, and the approximations of all parameters are given.

When the absolute criterion of the convergence of the *U*-function is fulfilled or when a declared number of iterations is reached, the minimization process terminates. In order to test the fit of the experimental points to the regression curve, the final table of curve fitting is printed.

EXPERIMENTAL

Spectrophotometer

A Spekol single-beam spectrophotometer (Zeiss, Jena) was equipped for photometric microtitrations with the multipurpose attachment TAL (*cf.* refs. 27, 29–31) with a thermostated cell and equipment for simultaneous measurement of pH. The design and function of TAL has been described previously.[31,32] The accuracy of the spectrophotometric measurements was checked with standard solutions of potassium chromate and copper(II) sulphate.[32] The pH of the titrand was recorded at the beginning and checked during the titration, with a Radiometer PHM 4d pH-meter (G202B glass electrode and saturated calomel electrode, calibrated with standard buffers[34]).

The titration cell was a 50-mm path-length cuvette, total volume 23 ml (type C, Zeiss, Jena). All the measurements were made at 25 ± 0·1°.

Burettes

A Metrohm E457 500-μl microburette was used, its polyethylene capillary tip being immersed in the titrand. Metal and indicator solutions were measured out with home-made microburettes[31] of 500 μl or 250 μl capacity, calibrated by weighing water delivered under medicinal paraffin (standard deviations for 25 deliveries of 200 and 100 μl were 0·3 and 0·2 μl, respectively).

Reagents and solutions

EDTA solution, 0·001M. Prepared in doubly distilled water. Standardized against twice recrystallized lead(II) chloride by photometric titration, using Naphthylazoxine 6S as indicator.

Naphthylazoxine 6S and SNAZOXS solutions, 0·001M. Both indicators were purified[35] and the effective concentration of indicator was determined by the molar-ratio method with copper.[35] The disodium salts of the indicators were fully protonated on a cation-exchanger column in H^+-form.

Zinc(II) solution, 0·001M. Prepared by dissolving 0·074 g of $Zn(NO_3)_2 . 6H_2O$ in water and diluting to 250 ml. Standardized by chelatometric titrations using Xylenol Orange as indicator.

Hexamine buffer, 0·04M. Adjusted to pH 6·0 with 0·05*M* nitric acid and to ionic strength 0·02 with 0·1*M* potassium nitrate. Purified by extraction with dithizone solution in carbon tetrachloride.

The solutions titrated with 0·001*M* EDTA always contained the same amount of individual components and the same sample volume was used. The solution titrated had a constant ionic strength of 0·01 and pH 5·80 adjusted with hexamine buffer and potassium nitrate, and temperature 25°. The solutions titrated had the same metal-ion concentration $c_M = 1·0 \times 10^{-5}M$ (except for investigation of effect of c_M) and the same indicator concentration $c_{In} = 1·0 \times 10^{-5}M$ (except for investigation of effect of c_{In}).

Procedure

Take an aliquot of metal-ion solution and a suitable portion of indicator stock solution in a calibrated 50-ml flask, add a few ml of buffer solution and make up the volume to 50 ml with doubly distilled water. Transfer 20·00 ml of this mixture into the titration cell, place this in the apparatus and adjust the equipment. Fill the reference cell with a solution containing no indicator but the same amounts of all other components. Place the reference cell in the light-beam and adjust the meter scale (0 and 100% *T*). Put the measuring cell into position and take readings of absorbance (or transmittance) at the beginning of the titration and at every 10 μl (ever 5 μl in the vicinity of the end-point) of titrant added, until constant absorbance is reached. About 35 points are usually read.

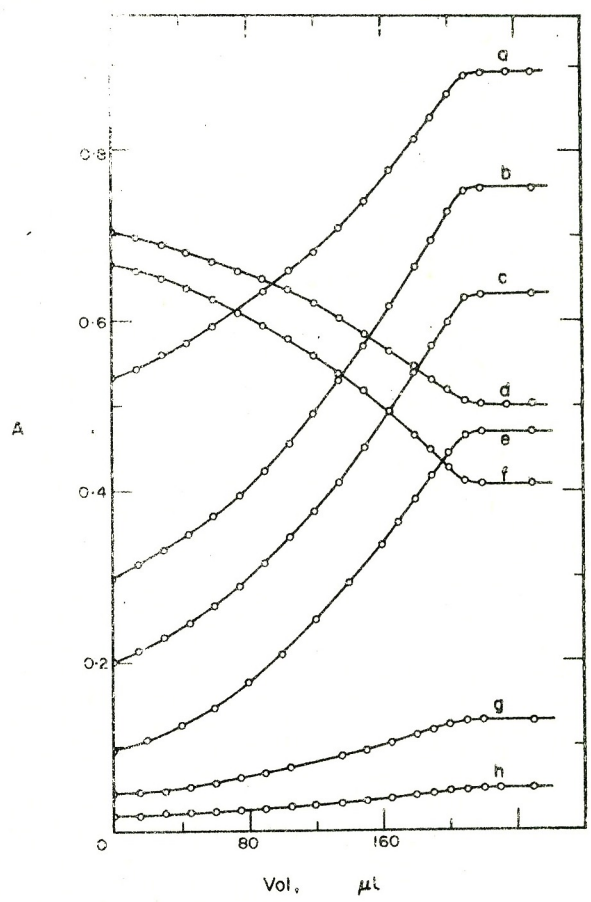

Fig. 3. Photometric titrations of zinc(II) with 0·001*M* EDTA, using Naphthylazoxine 6S as indicator, at various wavelengths. $c_{In} \approx 10^{-5}M$, $c_{Zn} = 1·045 \times 10^{-5}M$, pH 5·80 (hexamine), I = 0·01 (KNO_3), volume ≈ 20 ml, d = 50·0 mm, temperature 25°. Theoretical equivalence point: 0·209 ml. Wavelengths, *nm*: (*a*) 500, (*b*) 525, (*c*) 540, (*d*) 450, (*e*) 550, (*f*) 425, (*g*) 565, (*h*) 575. Evaluations of the curves are listed in Table 2.

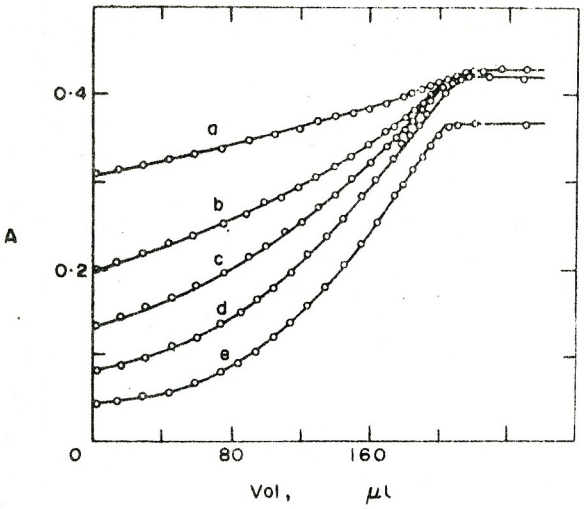

Fig. 4. Photometric titrations of zinc(II) with 0·001*M* EDTA, using SNAZOXS as indicator, at various pH values. $\lambda = 550$ nm, $c_{Zn} = 1{\cdot}060 \times 10^{-5}M$, $c_{In} \approx 10^{-5}M$, $I = 0{\cdot}01$ (hexamine + KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Theoretical equivalence point: 0·212 ml, value of pH (adjusted with 1*M* HNO_3): (*a*) 4·72, (*b*) 5·34, (*c*) 5·80, (*d*) 6·23, (*e*) 6·84. Evaluations of the curves are listed in Table 3.

RESULTS AND DISCUSSION

Photometric titrations of zinc(II) and lead(II) with 0·001*M* EDTA, using Naphthylazoxine 6S and SNAZOXS as indicators, were chosen as models because formation of MIn_2 complexes is expected. Both indicators form predominantly simple MIn_2 type complexes[27] and have been studied in our laboratory for several years. End-points were located by graphical extrapolation and also by numerical analysis of the curves. During the minimization process log K_{MY} was kept constant at a value taken from tables because MY was too stable for determination of K_{MY} to be considered certain.

The effect of choice of wavelength is demonstrated in Fig. 3. Only one component should absorb significantly so the difference between the molar absorptivities of the free indicator ϵ_{In} and its complex ϵ_{MIn_N} should be as great as possible. The graphical and numerical evaluations of the curves are shown in Table 2. The end-points evaluated numerically are slightly but negligibly earlier than those obtained graphically. The evaluation of the indicator concentration and stability constant of the indicator complex was not substantially influenced by the choice of wavelength. The standard deviations of both parameters had low values. In some cases subroutine Letag was not able to determine a standard deviation.[26]

The effect of pH is shown in Fig. 4 and Table 3. At low pH the difference between the absorbance of the free form of the indicator and its complex is reduced and the sharpness of the titration curve is also decreased. However, at pH higher than 6·4, acid–base reactions interfere with the complexation equilibria. The end-points of the five curves evaluated were not substantially influenced except for those at the two extreme pH values 4.42 and 6·85 and were in good agreement with the equivalence point.

The evaluation of the indicator concentration was also not influenced by pH. Corrections for $\alpha_{In(H)}$ at various pH values led to the same value of K_{MIn_2}.

The influence of indicator concentration is demonstrated in Fig. 5. The use of more indicator markedly

Table 2. Calculated results for the titration data in Fig. 3 [$\log\alpha_{In(H)} = 1{\cdot}47$; log $K_{MY} = 16{\cdot}15$ (*cf.* Ref. 27); $\log \alpha_{Y(H)} = 4{\cdot}97$]

λ, *nm*	End-point volume, *ml* Graphical	Numerical	Rel. dev. %	$-\log c_{In}$	log K_{MIn_2}
425	0·211	0·2091 ± 0·0021	0·05	4·91 ± 0·03	13·04 ± 0·09
450	0·212	0·2086 ± 0·0011	−0·19	4·91	12·82
500	0·210	0·2095 ± 0·0017	0·24	4·85	13·06 ± 0·14
525	0·209	0·2091 ± 0·0012	0·05	4·98	13·91 ± 0·19
540	0·210	0·2087 ± 0·0018	−0·14	4·89 ± 0·04	13·03 ± 0·12
550	0·210	0·2081 ± 0·0012	−0·43	4·90 ± 0·05	13·01 ± 0·13
565	0·208	0·2083 ± 0·0018	−0·33	4·91	13·07 ± 0·14
575*	0·220	0·2173 ± 0·0019	−0·81	4·91 ± 0·05	13·29 ± 0·14
Average	0·210	0·2086 ± 0·0005	−0·19	4·91 ± 0·04	13·13 ± 0·18

* Results at this wavelength were not taken into account for the average value.

Table 3. Calculated results for the titration data in Fig. 4 [log $K_{MY} = 16{\cdot}15$ (*cf.* ref. 27)]

pH	log α_{MIn_2}	log α_{MY}	End-point volume, *ml* Graphical	Numerical	Rel. dev. %	$-\log c_{In}$	log K_{MIn_2}
4·72	2·29	7·01	0·210	0·2052 ± 0·0015	−2·74	4·87 ± 0·05	12·15
5·34	1·68	5·81	0·210	0·2168 ± 0·0023	2·26	5·00	12·55
5·80	1·23	4·99	0·210	0·2107 ± 0·0015	−0·61	5·00	12·27
6·23	0·84	4·30	0·210	0·2126 ± 0·0012	0·28	4·91	12·55
6·84	0·39	3·51	0·208	0·2140 ± 0·0032	0·96	4·80	12·09
Average			0·210	0·2119 ± 0·0031	−0·05	4·92 ± 0·09	12·31 ± 0·24

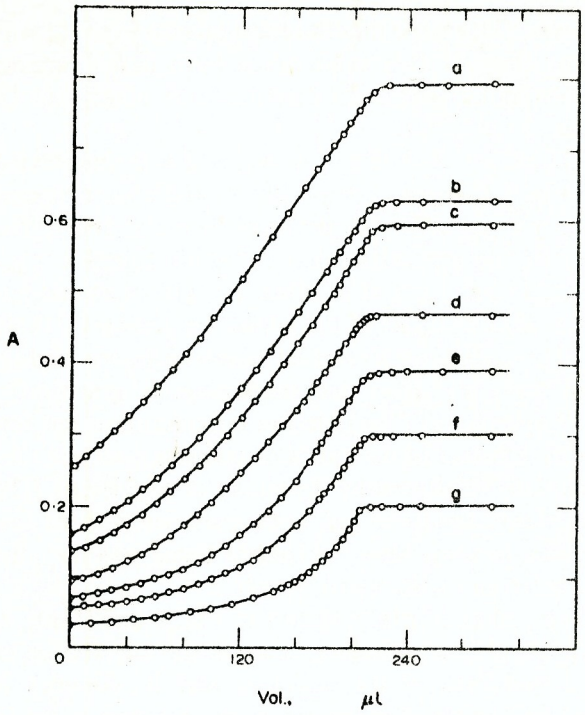

Fig. 5. Photometric titrations of zinc(II) with 0·001*M* EDTA, using Naphthylazoxine 6S, with various concentrations of the indicator. $\lambda = 555$ nm, $c_{Zn} = 1{\cdot}065 \times 10^{-5}M$, pH 5·75 (hexamine). $I = 0{\cdot}01$ (KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Theoretical equivalence point: 0·213 ml; indicator concentration, *M*: (*a*) $1{\cdot}78 \times 10^{-5}$, (*b*) $1{\cdot}41 \times 10^{-5}$, (*c*) $1{\cdot}20 \times 10^{-5}$, (*d*) $1{\cdot}0 \times 10^{-5}$, (*e*) $0{\cdot}79 \times 10^{-5}$, (*f*) $0{\cdot}60 \times 10^{-5}$, (g) $0{\cdot}40 \times 10^{-5}$.

improves the shape of the titration curve, mainly in the linearity before the end-point. The optimum amount to use is related to the accuracy in reading the absorbance. The indicator concentrations evaluated correspond to the actual analytical concentrations of the indicator in the solutions titrated. The indicator concentration does not influence the position of the end-point or the value of the stability constant of the indicator complex.

The effect of the metal-ion concentration is demonstrated in Fig. 6. The evaluated end-points were in agreement with the theoretical values. No marked difference was found between the graphical and numerical approach. The SIGY value[26] of the best curve fitting for a set of titrations of zinc(II) with SNAZOXS as indicator had the same value as the standard deviation of the absorbance, *i.e.*, 0·0035. The worst curve fitting was found for a family of lead(II) titrations, with the same indicator. Higher SIGY values indicate that the experimental points are subject to greater errors or that the curve does not correspond to the suggested mathematical model, *e.g.*, there may be consecutive complex-forming equilibria.

CONCLUSIONS

The application of the program is limited. When the shape of the titration curve contains a long linear part before the equivalence point the estimation of the parameter log $K_{MY,cond}$ is not reliable. This parameter and log $K_{MIn_N,cond}$ are ill-conditioned in the model. In such cases the log $K_{MY,cond}$ value is kept constant during the minimization process.

The value of $c_{In}^2 K_{MY}$ determines the curvature of the titration curve before the equivalence point and $c_M K_{MY}$ can only be determined from the titration

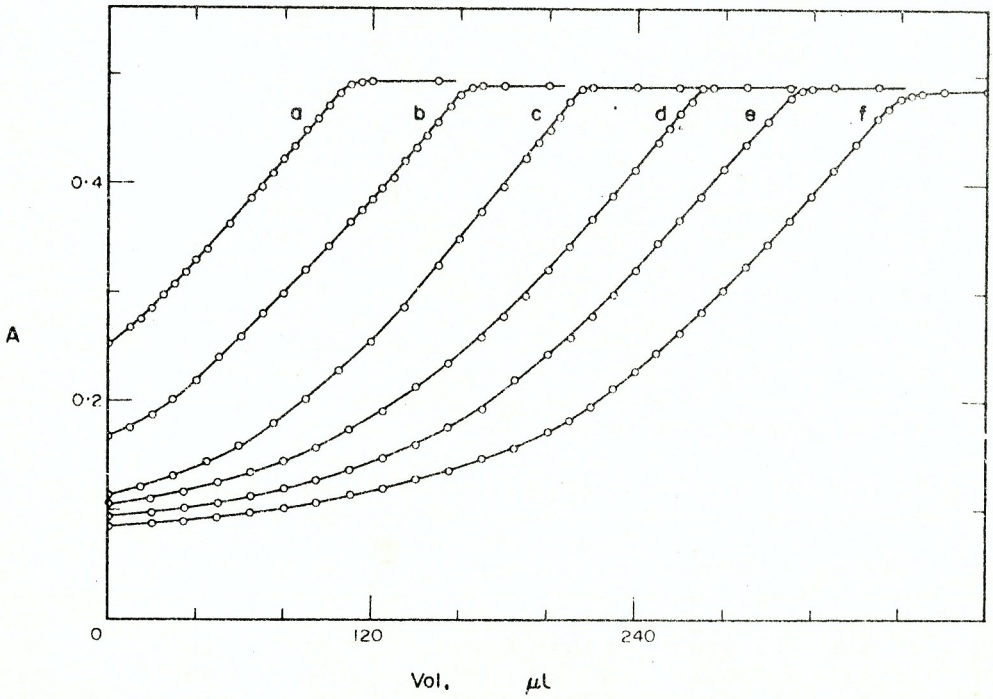

Fig. 6. Photometric titration of lead(II) with 0·001*M* EDTA, using Naphthylazoxine 6S as indicator, for various metal concentrations. $\lambda = 555$ nm, $c_{In} \approx 10^{-5}M$, pH 5·75 (hexamine) $I = 0{\cdot}01$ (KNO_3), volume ≈ 20 ml, $d = 50{\cdot}0$ mm, temperature 25°. Metal concentration c_{Pb}, *M*: (*a*) $0{\cdot}56 \times 10^{-5}$, (*b*) $0{\cdot}83 \times 10^{-5}$, (*c*) $1{\cdot}07 \times 10^{-5}$, (*d*) $1{\cdot}35 \times 10^{-5}$, (*e*) $1{\cdot}55 \times 10^{-5}$, (*f*) $1{\cdot}78 \times 10^{-5}$.

curve with an acceptable accuracy when the curvatures are large. In that case, however, the titration itself is inaccurate and no longer of analytical interest. When, as commonly in practice, we deal with "good" curves, it will hardly be possible to determine K_{MY}, and only K_{MIn_N} can be determined in particular cases (no impurities giving interactions, MIn_N the only indicator complex formed in solution, $c_{In}^2 . K_{MIn_N} < 10^4$).

A preliminary analysis of the metal-indicator and the metal-titration reagent system is necessary in order to obtain preliminary information on the stoichiometric coefficient N, the absence of consecutive equilibria, and all the competing equilibria occurring in the solution. For the NCHEL-LETAG program to be usable for evaluation of the titration curve it is necessary that the indicator complex predominantly formed is of the type MIn_N.

Acknowledgement—The authors wish to express their gratitude to Ing. Václav Říha and Doc. Ing. Stanislav Kotrlý, C.Sc. for valuable discussions on the experimental part of this contribution.

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