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Application of LETAGROP to spectrophotometric data, for testing models and adjusting equilibrium constants

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ABSTRACT

Table 4 gives special blocks for the minimizing program LETAGROP that allow one to deduce the "best" equilibrium model from spectrophotometric data for a series of equilibrium solutions. The LETAGROP method can also treat cases with several polynuclear and mononuclear species and is not restricted as to the number of species (provided of course there is a sufficient number of independent data). The program, called SPEFO should also be applicable to data which follow an equation of the same type as (1): other spectral data, conductance etc.

Examples are given of the application of LETAGROP to data from the literature.

Spectrophotometric measurements have often been used for equilibrium analysis, that is for deducing the nature and formation constants of the various species present in equilibrium solutions. Typically the data contain the absorptivity values, E, for a certain number (say N_λ) of wavelengths in each one of a certain number (N_{soln}) of equilibrium solutions, of known analytical composition.

We assume that Beer's law is valid and that for each solution and wavelength, E may be expressed by

$$E = \Sigma c_i \varepsilon_i \qquad (1)$$

In eqn (1), c_i is the concentration of species no i in this solution, ε_i is its molar absorptivity for this wavelength λ, and the sum is taken over all absorbing species.

In this paper, and the program, we use the older symbol E for absorptivity instead of the IUPAC symbol A, to avoid confusion with the total concentration A.

In real life, E is always measured for a band of wavelengths, narrow or broad, as determined by the properties of the filter or monochromator, or the line breadth of the spectral line used. In the following we shall nevertheless talk about "wavelength" when a band is meant, and the E and ε_i values are thus averages. We shall assume that the ε_i do not vary significantly with λ within the band; otherwise Beer's law may no longer be valid.

If one has already deduced the formulas of the species and their formation constants, say from emf data, and in addition has $E(\lambda)$ for a sufficient number of solu-

tions, then one might use the latter for deducing the values $\varepsilon_i(\lambda)$ for each species. On the other hand, one often wishes to—or even has to—use spectrophotometric data as the main basis for equilibrium analysis, i.e. for deducing the formulas and formation constants of the species present. This type of investigation has been subjected to certain limitations in the past.

For a good survey of the various methods—graphical and others—that have been suggested and applied up to 1961 we refer the reader to Rossotti and Rossotti (1961).

In a very simple case, met with for instance in the study of acid-base indicators, one of the components occurs only in two species and these are the only two absorbing species in the solutions. The treatment of spectrophotometric data in such a case is straight-forward.

Equilibria $A+B \rightleftharpoons AB$ where all the species may absorb, have been studied repeatedly, and some recent references are given below.

Two pioneering papers on spectrophotometric methods for studying series of mononuclear complexes ML_n ($n=1,2,3...$) were published independently in 1944. Jannik Bjerrum (1944) introduced the so-called principle of corresponding solutions. If a metal ion M forms only mononuclear complexes ML_n with a non-absorbing ligand L, and two solutions have the same values for $\varepsilon_M = E/[M]_{tot}$ for a series of wavelengths, then the solutions are likely to contain the various complexes in the same relative concentrations, and hence have the same concentration of free ligand [L]. If the ligand absorbs light, one may instead consider $(E-\varepsilon_L[L]_{tot})/[M]_{tot}$.

Olerup (1944) in his work on Cl^- complexes of Fe^{3+} and Fe^{2+}, made a critical survey of earlier methods, suggested and applied several new methods of data treatment. His method III is also based on the principle that the apparent ε_M, if necessary corrected for ε_L, is a function only of free [L].

Improved methods have been introduced by Fronaeus (1951) and by Newman and Hume (1957). Spectrophotometric work has given valuable information on many systems, especially on simple ones with few and mononuclear species. When there are more than three species, however, all these methods seem to run a certain risk of accumulating errors and none seems applicable to systems where polynuclear species of unknown composition are formed.

Computer programs have been suggested for treating spectrophotometric data on equilibria $A+B \rightleftharpoons AB$; the equilibrium constant and the molar absorptivities ε being adjusted to get the best fit, either by a search method for K (Conrow *et al.* 1964, Ramette 1967) or by a least squares treatment embracing both ε and K (Wentworth *et al.* 1967). Ropars and Viovy (1966) have applied a search method to a system with mixed mononuclear Cu complexes, but it is not clear how practical it would be in a more complicated case.

For a system with a number of species, some of which may be polynuclear, a general mathematical method has been suggested by Tan (1958). We have not seen it applied to any experimental data and fear that it would require a precision higher than really achieved in present-day spectrophotometry.

Application of LETAGROP

While we have been applying the minimizing program LETAGROP to various types of problems, it has repeatedly struck us that the LETAGROP method could be useful also for treating spectrophotometric data. It might be reasonably hoped

that LETAGROP would also be applicable to cases with a considerable number of species, polynuclear or mononuclear, and with two, three or more components. It might also be expected to find the best possible fit (as defined by minimizing a chosen error square sum U) for a given model, even with very bad initial guesses for the equilibrium constants. It might finally be helpful, just as for emf data, for deciding whether the addition of a new species would improve the fit significantly or not. Indeed, some of our friends now and then asked us to write a program for this purpose.

Because of the large number of molar absorptivity values $\varepsilon_i(\lambda)$ that must be adjusted together with the equilibrium constants in a system with many species present, and many wavelengths studied, it was a necessary prerequisite first to reorganize the main program of LETAGROP, as described in part 6.

The first practical application of LETAGROP to spectrophotometry came when our friend Dr Ants Teder presented us spectrophotometric data on polysulfides, which may be considered as ternary and possibly polynuclear complexes of H^+, S^{2-} and S^0. On this system we learned some of the special cautions one must take when working with spectrophotometric data.

We have later rewritten our special "polysulfide program" to make a more general program for three cases: (1) complexes A + B, the total concentrations (A, B) are known for each solution, (2) complexes A + B + C, the activity (free concentration) of A and the total concentrations of the other two components are known (a, B, C), (3) complexes A + B + C, only the total concentrations (A, B, C) are known. One may easily extend the program to cases with other types of information.

We have applied this program to some data taken from literature and compared the results of the LETAGROP program with those reached by the original authors by graphical or numerical methods. This does not mean that we consider our conclusions as more correct than those of the original authors. We are not experts in this field, and in order to get the most reliable information from a certain set of data one must combine the capacity of the computer to carry out an enormous number of calculations with the experience of the research worker. The latter can best judge what are the reasonable ways to weight the points (or in other words to define the function U to be minimized), which points may be excluded because they deviate too much by gross error, and which are the most likely causes of systematic error.

By the present paper we have wished to draw the attention of those interested to the existence of a program which is free from some limitations of earlier treatments (for instance as to the number or composition of the species formed) and which could, by collaboration with the judgment of experimental chemists in this field, be made into a powerful tool to extract more precise information from spectrophotometric data.

We also wish to point out that the program should be applicable to any type of data that follow an equation of the same type as (1), e.g. other types of spectral data, and conductivity data.

Data for input

When one writes a new computer program it is sometimes a good idea to start by stating what information the computer must have to do the job. In a LETAGROP program, this information is stored as members of certain arrays of fixed quantities (*ag*, *as*, *ap*, *ak*) and adjustable quantities (*k*, *ks*).

In the present case we must tell how many solutions we have data for ($N_{soln} = Np[1]$), and how many wavelengths ($N_\lambda = ag[1]$). In addition we must tell whether

we will give for each solution the absorptivity E or the molar absorptivity per B:

$$\varepsilon_B = E/B \tag{2}$$

In the present program this is done by setting $ag[2]=0$ if E, and $ag[2]=2$ if ε_B is given.

For each solution we must give the concentration data (A, B), (a, B, C) or (A, B, C) and the E or ε_B values for the N_λ various wavelengths. If data are missing for some wavelength this may be indicated by setting a negative number, say -1, which could not be an experimental value.

We must also state whether we know beforehand the molar extinction values for some species, either they are all 0 or we have exact values from separate measurements, say, for the pure component species. This information could conveniently be given together with the coefficients (p, q) or (p, q, r) in the formulas of these species.

The present program deals with a number of independently mixed solutions, and so we have found it expedient to give the data in the form of two groups: in the first group each solution corresponds to one data point, for which concentration data and E(or ε_B) values are given, the second group contains the information on the extinction values assumed to be known.

In the future one might wish, for convenience, a special program for spectrophotometric titrations, in which case there might be some reason for introducing analytical errors in each titration as independent group parameters, counting each titration as a separate group. This will give us two independent systems of groups. Whereas this program could surely be written, we have seen no strong reason to do it now.

For the chemical model to be treated one needs the usual information about composition (p, q, r) and estimated formation constants (β) of the complexes. As usual the guesses for β need not be very good.

As for E_{1lm} see eqn (5b).

Table 1 indicates how the data and parameter arrays are used in the present program, Table 2 gives special instructions for the input. Other *Rurik* values than those in Table 2 are used just as for other types of problems. For instance, by means of *Rurik* = 17, one may test whether the addition of some out of a series of possible new species would improve the fit significantly (part 7). As usual, it is advisable to apply *Rurik* = 2 at an early stage to get an "Uttåg" with tables of input data, and calculated deviations. Unusually large deviations often indicate points that should be checked for misprints or gross errors.

Table 3 gives a specific example, namely the input data for calculation on Ahrland's data (1949) on thiocyanate-uranyl complexes, which some reader might want to use as a test. It is up to the user to decide how much of the partial results he wants to see in print; this can be regulated by the use of Rurik = 12 (part 6).

Definition of error square sum U

By means of the control number *val*, the LETAGROP programs allow a choice between various definitions for the error square sum to be minimized in the calculations

$$U = \Sigma fel[val]^2 \tag{3}$$

Table 1. Use of arrays for invariable quantities (*ag*, *as*, *ap*, *ak*) and adjustable parameters (*k*, *ks*) in application of LETAGROP to spectrophotometric data.

A "+" indicates that the quantity is not given in the input but calculated by the program; in such cases it need not be "invariable" even if it is stored in, say the **ap** matrix,

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ag $= N_\lambda$, *ag*[2] (= 0, if E will be given, = 2 if ε_B will ge given), E_{lim}, $+N_{\text{soln}}$, $+N_{\text{tab}}$, $+N_E$
as = –
ap in group 1:
Typ = 1: A, B, $(E)_{N\lambda}$, $+(c[\text{ix}])_{14}$, +lna, +lnb
Typ = 2, 3*: log a (or A*), B, C, $(E)_{N\lambda}$, $+(c[\text{ix}])_{13}$, +lna, +lnb, +lnc,
ap in group 2:
Typ = 1: p, q, $(\varepsilon_{pq})_{N\lambda}$; Typ = 2, 3: p, q, r, $(\varepsilon_{pqr})_{N\lambda}$
k $= \beta_{pq(r)}$
ak = pot, p, q, (r), ... + *ak*[6] (= 1 if ε_{pqr} assumed to be known
= – 1 if ε_{pqr} are to be adjusted)
ks = – (none in input, defined in program as $\varepsilon_{pq(r)}$)

Table 2. Input for SPEFO = spectrophotometric version of LETAGROP.

The input contains two groups. In the first group the data (total concentrations, absorptivity for various λ) for each solution are treated as a separate point. In the second group, each point gives the composition and ε values for some species whose values are supposed to be known already. After reading the data, the program redefines the groups so that the data for each separate wavelength constitute a group. The output in Uttåg (Rurik = 2) again gives data for each solution separately.

Typ = 1. Data: **14**(Rurik), text, **9**(Rurik), 1(Typ), **6**(Rurik), 2(Ns), 3(Nag), 0(Nas), Nap($= 2 + N_\lambda$), N_λ, ag[2] (= 0 if E, = 2 if ε_B given), E_{lim}, N_{soln}, (A, B, $(E_\lambda)_{N\lambda})_{N\text{soln}}$, N_{tab}, (p, q, $(\varepsilon_{pq},_\lambda)_{N\lambda})_{N\text{tab}}$,

Variable input (Dagens spaning): **7**(Rurik), Nk, Nk, 3(Nak), (k, pot, p,$q)_{Nk}$, 0, 0,0,
8(Rurik), 2(Nok), stegbyt, start(ln$b$), tol(B/B_{tot}), start(ln$a$), tol(A)
3(Rurik), N, (ik,w)$_N$ (orders for variation of equilibrium constants), **5**, **5** (two shots) etc.

Typ = 2 (or 3*). Data: **14**, text, **9**, 2(or 3*,Typ), **6**(Rurik), 2(Ns), 3(Nag), 0(Nas), Nap(3 + N_λ), N_λ, ag[2] (= 0 if E, = 2 if ε_B given), E_{lim}, N_{soln} (log$a$ (or A*), B, C, $(E_\lambda)_{N\lambda})_{N\text{soln}}$, N_{tab}, $(p,q,r,(\varepsilon_{pqr(\lambda)})_{N\lambda})_{N\text{tab}}$

Variable input (Dagens spaning): **7**(Rurik), Nk, Nk, 4(Nak), (k,pot,p,q,$r)_{Nk}$, 0, 0, 0,
8(Rurik), 3(Nok), stegbyt, start(ln$b$), tol(B/B_{tot}), start(lnc), tol(C/C_{tot}), start(ln$a$), tol(A),
3, N, (ik,w)$_N$ etc.

One should not use Rurik = **11**, **19** or **20** since the program will automatically vary all unknown ε_i values for all wavelengths. In the data, if a value for E (or ε_B) is not available, it is replaced by a negative rumber, e.g. – 1.

In the present program two definitions are available. With *val* = 1, one uses the "absolute" errors

$$fel[1] = E_{\text{calc}} - E \text{ or } \varepsilon_{B,\text{calc}} - \varepsilon_B \tag{4}$$

depending on whether the absorptivity E or the molar absorptivity for B has been given, and with *val* = 2 one uses the "relative" errors

$$fel[2] = (E_{\text{calc}} - E)/E \text{ if } E > E_{\text{lim}}, \tag{5a}$$

$$(E_{\text{calc}} - E)/E_{\text{lim}} \text{ if } E \leqslant E_{\text{lim}} \tag{5b}$$

Table 3. Input for Ahrland's (1949) data on $SCN^- - UO_2^{2+}$. Semicolon is used here to separate various parts of input; in input cards only commas are given. Results, see Table 6.

```
14
U02 - SCN STEN AHRLANDS DATA ACS 1949
9, 1; 6, 2, 3, 0, 4; 2, 2, 10;
(group 1) 39 ; 0.020, 0.0951, 70.8, -1 ; 0.030, 0.0564, 121.4, -1 ; 0.050, 0.03216, 220.8, -1 ;
0.020, 0.0247, 93.8, -1 ; 0.030, 0.1608, 144.7, -1; 0.050, 0.00992, 242.9, -1 ;
0.020, 0.00673, 102.5, -1 ; 0.030, 0.00457, 152.0, -1 ; 0.050, 0.002947, 249.0, -1 ;
0.200, 0.096, -1, 69.5 ; 0.300, 0.0654, -1, 104.5 ; 0.400, 0.0509, -1, 135.1 ;
0.050, 0.1044, -1, 18.63 ; 0.075, 0.067, -1, 31.10 ; 0.100, 0.0504, -1, 42.9 ;
0.150, 0.03373, -1, 64.7 ; 0.200, 0.02678, -1, 83.7 ; 0.300, 0.0197, -1, 116.5 ;
0.400, 0.01583, -1, 145.1 ; 0.010, 0.1045, -1, 3.87 ; 0.020, 0.0602, -1, 8.98 ;
0.030, 0.03913, -1, 14.57 ; 0.050, 0.02495, -1, 24.92 ; 0.075, 0.01673, -1, 37.49 ;
0.100, 0.01341, -1, 48.9 ; 0.150, 0.00966, -1, 70.2 ; 0.200, 0.00765, -1, 88.4 ;
0.300, 0.00569, -1, 121.6 ; 0.400, 0.00463, -1, 149.7 ; 0.010, 0.02801, -1, 5.22 ;
0.020, 0.01673, -1, 10.75 ; 0.030, 0.01174, -1, 16.35 ; 0.050, 0.00778, -1, 26.85 ;
0.075, 0.00541, -1, 39.39 ; 0.100, 0.00422, -1, 50.5 ; 0.150, 0.003122, -1, 71.8 ;
0.010, 0.00783, -1, 5.83 ; 0.020, 0.00490, -1, 11.53 ; 0.030, 0.00346, -1, 16.70 ;

(group 2) 2 ; 1, 0, 0, 0 ; 0, 1, 0, 0 ;
7, 3, 3, 3; 5.7, 0, 1, 1 ; 5.5, 0, 2, 1 ; 1.5, 1, 3, 1 ; 0, 0, 0 ;
8, 2, 0.4 ; -3, 3_10 - 7 ; -5, 3_10 - 8 ;

The rest is up to the user ; here is an example:
12, -1 ; 3, 0 ; 5, 2 ;
3, 3, 1, 0.2, 2, 0.2, 3, 0.2 ; 4, 0.2 ;
5, 5, 5, 13, 2, -1 ;
```

The quantity $E_{\lim}$ which is given as ag[3] may be chosen by the chemist's judgment; if the ε_B are given, (5a) and (5b) should be changed correspondingly.—Other definitions of *fel*[*val*] and hence U could be added, if this were thought desirable.

Function of program

Table 4 gives the text of the parts in LETAGROP that must be added for treating spectrophotometric problems: the block PUTS, and the block UBBE for calculating U. UBBE contains the package of procedures, BDTV, for equilibrium calculations, which was given in full in part 8. They contain a few quantities that may be superfluous in the present case, but we have chosen for convenience to use exactly the same procedures.

In the input and output it is convenient to give the data (concentrations, measured and calculated E) for each solution separately. In the calculations, on the other hand, the data for each wavelength should be treated as a separate group, with the ε_{pq} or ε_{pqr} as the group parameters k_s. The program makes the necessary rearrangement by itself: in particular it finds out, in the procedure Tabkoll, which ε_{pqr} values are already assumed to be known so that they will not be adjusted.

In the procedure Werda there is an extra check to prevent that one tries to adjust the ε_{pqr} values for any species whose formation constant is assumed to be zero, since a change in the ε_{pqr} of a non-existent species could not influence U, and the calculations would hence get stuck.

The adjustment of parameters is made at two levels, as described in part 6. The

Table 4. PUTS and UBBE for SPEFO (spectrophotometric version of LETAGROP).
Parts of UBBE are common to programs containing "BDTV" and are given in part 8, Table 1.

```
PUTS:     begin integer Nlam, Nsoln, Ntab, Rsoln ;
          if Rs = 0 then Napa: = Nap + 16 ; if Rs < 2 then goto DATA;
          Rs1: = 1 ; Rs2: = ag[1] ; Ns: = Nlam: = Rs2 ; Nsoln: = Np[1] ; ag[4]: = Nsoln ;
          Ntab: = Np[2] ; ag[5]: = Ntab ; Poskis: = true ; ag[6]; = 0 ;
          for Rs: = Rs1 step 1 until Rs2 do begin Np[Rs]: = 0 ;
            for Rsoln: = 1 step 1 until Nsoln do
              if ap[Napa × Rsoln − 16 − Nlam + Rs] ⩾ 0 then begin Np[Rs]: = Np[Rs] + 1 ;
                  ag [6]: = ag[6] + 1 end end ;
          for Rs: = 1 step 1 until Rs2 do for i: = 1 step 1 until 13 do begin ks[Rs,i]: = 0 ;
                  darks [Rs,i]: = darks2[Rs,i]: = − 1 end ;
          goto KNUT end PUTS ;
UBBE:     begin real Atot ..... t[1:20] ; = part 8
          real Elim ; integer Nlam, Nsoln, Ntab, Rlam, Rsoln ; Boolean Molex ;
          real array Ebert, felut[1:15] ;
          switch Haltab: = Tab1, Tab2, Tab3 ; switch Huvud: = Huvud1, Huvud2, Huvud3 ;

          procedures BDTV = part 8

procedure Espek ; begin m: = Rsoln × Napa − 16 ; Btot: = ap[m − Napa + 18]; Eber: = 0 ;
          E = ap [m − Nlam + Rlam] ;
          if E < 0 then Eber: = E else begin for ix: = 1 step 1 until Nx + Nkom do Eber: =
                  Eber + ap[m + ix] × ks[Rlam,ix] ;
            if Molex and Btot > 0 then Eber: = Eber/Btot end ;
          fel[1]: = Eber − E ;
          fel[2]: = if E > Elim then fel[1]/E else fel[1]/Elim
          end Espek ;
procedure Komin(Nkom) ; integer Nkom ; begin c[Nx + 1]: = exp(lna) ;
          if Nkom > 1 then c[Nx + 2]: = exp(lnb) ; if Nkom > 2 then c[Nx + 3]: = exp(lnc) ;
          cell: = Rsoln × Napa − 16 ;
          for ix: = 1 step 1 until Nx + Nkom do ap[cell + ix]: = c[ix] end Komin ;
procedure Tabkoll ; begin Nks: = Nx + Nkom ;
          for i: = 1 step 1 until Nkom do begin p[Nx + i]: = q[Nx + i]: = r[Nx + i]: = 0 ;
                  beta[Nx + i]: = 1 end;
          p[Nx + 1]: = 1 ; if Nkom > 1 then q[Nx + 2]: = 1 ; if Nkom > 2 then r[Nx + 3]: = 1 ;
          for ix: = 1 step 1 until Nx + Nkom do begin Bra: = false ; ak[ix,6]: = − 1 ;
            for m: = 1 step 1 until Ntab do begin cell: = Napa × (Nsoln + m − 1) ;
              if entier(ap[cell + 1] + 0.01) = p[ix] then Bra: = true ;
              if Nkom > 1 and entier (ap[cell + 2] + 0.01) ≠ q[ix] then Bra: = false ;
              if Nkom > 2 and entier (ap[cell + 3] + 0.01) ≠ r[ix] then Bra: = false ;
              if Bra then begin ak[ix,6]: = 1 ;
                for Rlam: = 1 step 1 until Nlam do ks[Rlam,ix]: = ap[cell + Nkom + Rlam] ;
                  Bra: = false end end end ;
          Bra: = true end Tabkoll ;
procedure Werda ; begin for Rlam: = 1 step 1 until Nlam do Niks[Rlam]: = 0 ; m: = 0 ;
          for ix: = 1 step 1 until Nx + Nkom do begin Bra: = false ;
            if lnbeta[ix] ⩽ − 400 then Bra: = true ;
            if ak[ix,6] > 0 then Bra: = true ;
            if not Bra then begin m: = m + 1 ;
              for Rlam: = 1 step 1 until Nlam do begin Vaks[Rlam,m]: = ix ; Niks[Rlam]: = m
                  end end end ;
          Npunkt: = ag[6] end Werda ;

          Nlam: = ag[1] ; Nkom: = if Typ = 1 then 2 else 3 ;
          if ag[2] > 1 then Molex: = true else Molex: = false ;
          Elim: = ag[3] ; Nsoln: = ag[4] ; Ntab: = ag[5] ; dirt: = 0 ;
          if Tage then goto Uber ;
          for i: = 1 step 1 until N do begin ik: = ivar[i] ;
```

```
            if Orvar = 9 and k[ik] < 100 × ag[7] then begin Orvar: = 8 ; k[ik]: = 0 end ;
            if k[ik] ⩽ 0 then begin k(ik]: = 0.0005 × kc[i] ; if N = 1 then ag[7]: = k[ik] end end ;
          Betain(1,Nk) ; Koks: = true ; if Orvar = 0 or Orvar = −2 then Tabkoll ;
          Nskott: = if Orvar = 0 then 2 else 1 ;
          if Rurik = 2 then begin Rsoln: = 0 ; goto Huvud[Typ] end ;
          Werda ; Rsoln: = 0 ;
Nyl:      Rsoln: = Rsoln + 1 ; cell: = (Rsoln − 1) × Napa ;
          if Rsoln ⩽ Nsoln then goto Haltab [Typ] ;
          if Rurik ≠ 2 then goto SÄRK ;
          Rsoln: = 0 ; U: = 0 ;
Skriv:    Rsoln: = Rsoln + 1 ; if Rsoln > Nsoln then goto Slut ;
          cell: = (Rsoln − 1) × Napa ;
          for Rlam: = 1 step 1 until Nlam do begin Espek ; Ebert[Rlam]: = Eber ;
          felut[Rlam]: = fel[val]; U: = U + fel[val]↑2 end ;
          goto Uttåg ;
Tab1:     Atot: = ap[cell + 1] ; Btot: = ap[cell + 2] ;
          Valhal (3,Napa − 1) ; Komin(Nkom) ; goto Nyl ;
Tab2:     lna: = ln10 × ap[cell + 1] ; Btot: = ap[cell + 2] ; Ctot: = ap[cell + 3] ;
          Valhal (2, Napa − 2) ; Komin(Nkom) ; goto Nyl ;
Tab3:     Atot: = ap[cell + 1] ; Btot: = ap[cell + 2] ; Ctot: = ap[cell + 3] ;
          Valhal (3, Napa − 2) ; Komin(Nkom) ; goto Nyl ;
Huvud1:   output(61,'/5B'ATOT',7B,'BTOT'/,5B,'E',11B,'EBER',7B,'FEL(VAL)") ; goto Nyl;
Huvud2:   output(61,'/5B,'LOGA',8B,'BTOT',8B,'CTOT',/,5B,'E',11B,'EBER',7B'FEL(VAL)");
          goto Nyl ;
Huvud3:   output(61,'/5B,'ATOT',8B,'BTOT',8B,'CTOT',/,5B,'E',11B,'EBER',7B,'FEL(VAL)");
          goto Nyl ;
Uttåg:    m: = Napa − 16 − Nlam ; output(61,'/') ;
          for i: = 1 step 1 until Nkom do output(61,' − 3ZD.6D', ap[cell + i]) ;
          i: = 3 ;
          for Rlam: = 1 step 1 until Nlam do begin i: = i + 1 ;
            if i > 3 then begin output(61,'/') ; i: = 1 end ;
            output(61,'3( − 5ZD.3D)',ap[cell + m + Rlam], Ebert[Rlam],felut[Rlam]) ;
          goto Skriv ;
Uber:     U: = 0 ; Rlam: = Rs ;
          for Rsoln: = 1 step 1 until Nsoln do begin Espek ; U: = U + fel[val]↑2 end ;
Slut:     if Skrikut = 1 or (Skrikut = 0 and not Tage) or (Prov and not (Tage and Skrikut < 0))
                    or Rurik = 1 or Rurik = 2 then begin
            UVAR ; if Prov then output(61,'/') end ;
          goto UBBEUT end UBBE ;
FINAL:    end LETAGROP ;
```

equilibrium constants for the formation of complexes are varied at an upper level. For each set of equilibrium constants, $\vec{\mathbf{k}}$ (common parameters) the computer calculates the concentrations of the various species in each solution. This is done at the label Haltab, by means of the procedure Valhal (part 8), and the concentration values are stored in reserved cells of the *ap* array using the procedure Komin.

When the concentrations are thus known, the computer uses SÄRK (part 6) and the orders after the label Uber in UBBE to calculate, for each wavelength, the contribution to U for a systematically chosen number of sets of the k_s ($=\varepsilon_{pqr}$). By assuming a second-degree surface it then calculates the values for ε_{pqr} that give the minimum contribution to U from that wavelength. Since equation (1) is linear in the ε_i, the surface $U(\vec{\mathbf{k}}_s)$ should be exactly a second degree surface, and hence one should get the exact minimum in one "shot" whatever starting values one chooses for $\mathbf{k}_s$, and whatever steps one uses in the variation, with the limitations given by the word-length of the computer. We have found it quite sufficient to start the very first

"shot" with the guess 0 for all the k_s, and to vary them by the step 1, which is given by the *darks* = −1 set automatically on reading the parameters in LÄSK. After this shot, of course, the computer has values of the right order for the k_s and their standard deviations and these are improved in one more shot (*Nskott* = 2). After this, one shot is enough (*Nskott* = 1).

After one shot for each wavelength, the computer sums up the minimum error square sums obtained, and thus gets the lowest value for U that can be obtained with that set of common parameters $\vec{\mathbf{k}}$. The set $U(\vec{\mathbf{k}})$ obtained is treated as usual to find the minimum, if necessary eliminating negative, or "insignificant" parameter values by means of MIKO (part 7).

The present program provides space for storing the concentrations of 13 species in the matrix **ap**. At present this seems ample since usually complex chemists are treating cases with at most 4–6 species but if the need to increase the number were to arise, this could easily be done by increasing the quantity *Napa* in PUTS.

We must also observe that negative values for ε_{pqr} are not realistic so that one could not accept a minimum that requires some ε_{pqr} value to be negative. On the other hand, no difficulties arise if equation (1) is applied with negative ε_{pqr} values, and so the whole calculation can be carried out up to GROP without any need to use the procedures Komner and PLUSKA, which are otherwise used to keep parameters positive. Only at the end, when the minimum is calculated, it is checked whether some k_s (ε_{pqr}) come out negative, in which case MIKO is applied to find the set of ε_{pqr} that gives the lowest U values while all are zero or positive. In the midst of the calculations, in LETA, a lower U value is not accepted as the lowest value $U_{\min}$, if it requires some ε_{pqr} to be negative; it is used, however, in the calculation of the surface $U(\mathbf{k}_s)$. To ensure that the $\mathbf{k}_s$ are treated as described, a Boolean *Poskis* is used, which is **true** for spectrophotometric problems, but **false** for others.

When SPEFO is applied to other types of data that follow (1), such as optical rotation data, negative E and ε_i values may occur. An obvious remedy is adding a sufficiently large constant value, ε_0, to say, ε_B, hence adding $B\varepsilon_0$ to E and $q\varepsilon_0$ to ε_{pqr}.

Peculiarities in performance

In our experience up to now with the spectrophotometric version of LETAGROP we have noticed two peculiarities:

(1) It seems more important than in any other case we have met with that one uses quite low tolerance values for solving the equations; these tolerances are given after *Rurik* = 8. If too large tolerances are used, the U values scatter, and the computer may happen once to find a low value for U but in the following variation it finds only U values that are higher by, say, a factor of 1.00001, so that it never gets an acceptable minimum with the normal value $tolU = 10^{-6}$. In some cases the computer thus got caught in a loop when we set the tolerances as large as 10^{-5} but it found a minimum quite normally if we decreased the tolerances to 10^{-7}.

Another way out is to increase *tolU* to, say, 10^{-4}, using *Rurik* = 4.

The difficulties met by Conrow *et al.* (1964) may have had the same causes; at any rate, once one is aware of the cause, the remedy is easily found.

(2) Suppose that a certain species (P, Q, R) absorbs strongly but has a very low formation constant, β_{PQR} so that its concentration is small compared with the concentrations of the reagents. Then, if one divides β_{PQR} by 10 and multiplies all ε_{PQR}

values by 10, one would get practically the same calculated E values. So, the value for U would be very little sensitive to changes in β_{PQR}.

On the other hand, if β_{PQR} is set exactly $=0$, the absorption ascribed to that species would disappear, and the value for U would rise discontinuously to a higher value. So, if only $k_1=\beta_{PQR}$ is varied, the function $U(k_1)$ is discontinuous at 0. For a species with a low formation constant (or even dubious existence) on approaching 0 one would try to draw a parabola through two points on the continuous curve and one (at $k_1=0$) above it.

The standard treatment in ENSAM then may need 8–10 attempts, with decreasing steps around 0, until an acceptable minimum is found; since the program is working quite fast, this did no great harm in the cases we have studied. In other cases we might imagine that it could be a good idea—once some species has been recognized to be of the type described—to give its formation constant a low and constant value, thus not to adjust it, but only to adjust its ε values. Hence the product $\beta\varepsilon$ can be obtained which is much more accurately defined than any of the quantities separately.

One might think of placing the point $U(0)$ on a continuous curve by never letting an equilibrium constant be exactly zero but letting it stop at, say, e^{-50}. We have tried this way but do not recommend it since it leads into other difficulties which it would take too much space to describe. (The curious reader may change -1000 to -50 in the procedure Betain and try for himself.)

The **for** statement before label Nyl in the beginning of UBBE is another way of preventing an equilibrium constant from becoming exactly zero. So far it has worked; *ag* [7] is a memory cell used for this special purpose.

Still another way of treating such cases would be to maximize the ε_i values, say, to 40,000 or some other reasonable value. One might then make some additions to MIKO, which would, for each set of equilibrium constants, search for the best agreement possible with all ε_i values confined between 0 and ε_{max}. We have so far seen no compelling reason to rewrite the program in that direction.

With more experience, there will surely be good reasons for adding refinements and safeguards to the program.

Application to literature data

Tables 5–9 show results obtained by application of the present program to some data from literature. They are all two-component systems with predominantly mononuclear complexes, since this is the type of systems that could be treated by earlier methods. Applications to systems with three components will follow e.g. in Ants Teder's work on polysulfides.

The LETAGROP results in the tables give the "best" values for the β and ε, followed by their standard deviations, $\sigma(\beta)$ or $\sigma(\varepsilon)$. The estimated error limits from graphical treatment by good workers, like those quoted, usually corresponds to about 3σ; in other publications we often give 3σ from the LETAGROP results but here σ is given.

Again, we do not insist that our values are "better" than those of the authors, but we think the tables illustrate the possibilities the method gives for a precise and objective (and also fast) treatment of spectrophotometric data. The tables are almost self-explanatory and we shall only make a few comments.

In all cases we have tried to adjust the parameters, using both "absolute" and

Table 5. Complex formation triphenylarsine (A) + Ag^+ (B) in methanol–water. Data of Olson and Bjerrum 1966, $\lambda_1 = 233$ nm, $\lambda_2 = 238$ nm, MeOH. Authors have measured ε_{10} and ε_{11} in separate experiments. Last columns show result of ignoring authors' ε_{11}. We assume $\varepsilon_{01}(Ag^+) = 0$.

	Authors	*val* = 1 (abs)	*val* = 2 (rel)	*val* = 1	*val* = 2	*val* = 1	*val* = 2
(a) 55.6 wt % MeOH (6 solutions)							
$\beta_1 \cdot 10^{-5}$	≈ 6.2	6.63 ± 0.68	5.47 ± 0.63	6.2	6.2	1.31 ± 0.57	0.56 ± 0.35
λ_1: ε_{10}	10100	10100	10100	10100	10100	10100	10100
ε_{11}	16500	16500	16500	16700 ± 230	16390 ± 290	21040 ± 260	27300 ± 500
λ_2: ε_{10}	10800	10800	10800	10800	10800	10800	10800
ε_{11}	16500	16500	16500	16600 ± 200	16330 ± 270	20410 ± 270	25900 ± 600
$U_{abs} \cdot 10^5$	4.66	4.50	—	4.21	—	1.88	—
$U_{rel} \cdot 10^3$	8.99	—	8.25	—	8.57	—	3.47
(b) 75.4 wt % MeOH, 6 solutions							
$\beta_1 \cdot 10^{-5}$	≈ 5.0	5.05 ± 0.22	4.84 ± 0.26	5.0	5.0	2.02 ± 1.14	1.65 ± 1.03
λ_1: ε_{10}	10100	10100	10100	10100	10100	10100	10100
ε_{11}	16000	16000	16000	16020 ± 90	15950 ± 110	17760 ± 120	18320 ± 155
λ_2: ε_{10}	10900	10900	10900	10900	10900	10900	10900
ε_{11}	16100	16100	16100	16110 ± 75	16070 ± 90	17640 ± 100	18160 ± 130
$U_{abs} \cdot 10^6$	9.30	9.26	—	9.24	—	7.97	—
$U_{rel} \cdot 10^3$	1.38	—	1.33	—	1.34	—	1.12

Table 6. Complex formation SCN^-(A) + UO_2^{2+}(B), data of Sten Ahrland 1949. Wavelengths λ_1 (366 nm, 9 solutions), λ_2 (436 nm, 30 solutions). ε_{10} (for SCN^-) negligible. In original, measured ε_{01} (for UO_2^{2+}) was subtracted from ε_B, hence given "ε_{pq}" are $\varepsilon_{11} - \varepsilon_{01}$, $\varepsilon_{21} - \varepsilon_{01}$, $\varepsilon_{31} - \varepsilon_{01}$, and "$\varepsilon_{01}$" is assumed to be 0 for λ_1 och λ_2.

	val = 1	Author's β	*val* = 2	*val* = 1 abs.errors	*val* = 2 rel.errors
β_1		5.7(±0.3)		5.37 ± 0.13	5.46 ± 0.11
β_2		5.5(±1)		9.05 ± 1.5	9.06 ± 1.1
β_3		15(±5)		6.4 ± 3.4	5.5 ± 3.2
λ_1: ε_{11}	964 ± 17		975 ± 9	1005 ± 26	1001 ± 15
ε_{21}	3510 ± 1110		2740 ± 660	2490 ± 990	2140 ± 660
ε_{31}	3400 ± 5800		7500 ± 3700	1200 ± 19900	10100 ± 16600
λ_2: ε_{11}	111.0 ± 0.8		108.45 ± 0.33	114.4 ± 0.7	111.7 ± 0.3
ε_{21}	308 ± 9		342 ± 7	217.4 ± 4.1	230.6 ± 3.6
ε_{31}	257 ± 7		227 ± 8	469 ± 13	486 ± 18
U_{abs}	5.75		—	4.45	—
$U_{rel} \cdot 10^4$	—		10.96	—	8.06
σ(fel[2])					0.0052

"relative" errors (eqn 4, 5) in defining the error square sum U. The same values for β and ε have been obtained within the 3σ limits (and usually much closer). It is up to the experimentalist to judge in each case which weighting is preferable.

In Olson and Bjerrum's measurements on triphenylarsine-Ag^+ (Table 5) there was only one β value to adjust and all the ε values were known from separate measurements. The table shows attempts to adjust only β, to adjust ε_{11}, if β is assumed to be known, and to adjust both ε_{11} and β. The latter means that one ignores the meas-

Table 7. Complex formation $Cl^-(A) + UO_2^{2+}(B)$, data of Sten Ahrland 1951. 8 wavelengths, 3 solutions. Individual ε_{pq} values omitted here.

	Author's β	*val* = 1	*val* = 2	*val* = 1	*val* = 2
$\beta_1 \cdot 10$	5(±3)	5.95 ± 0.46	5.10 ± 0.75	27 ± 19	26 ± 15
$\beta_2 \cdot 10$	—	—	—	17 ± 14	19 ± 12
U_{abs}	77.39	59.30	—	18.37	—
$U_{rel} \cdot 10^4$	50.72	—	50.66	—	8.74
σ(fel[2])			0.018		0.012

Table 8. Complex formation glycollate ion $(A) - Cu^{2+}(B)$, data of Fronaeus 1948, p.121, one wavelength (295 nm), 28 solutions, $(E - \varepsilon_{10}A)$ given, hence "ε_{10}" is assumed to be 0, and "ε_{p1}" $= \varepsilon_{p1} - p\varepsilon_{10}$. In the calculations, ε_{01} (for Cu^{2+}) was also adjusted; it is presumably negligible.

	val = 1	Author's β values	*val* = 2	*val* = 1 absolute errors	*val* = 2 relative errors
β_1		270(±30)		197 ± 35	190 ± 22
β_2		5000(±500)		3010 ± 630	3060 ± 540
$\varepsilon_{01}(Cu^{2+})$	2.2 ± 0.9		2.9 ± 0.8	0 ± 0.7	0.5 ± 0.7
ε_{11}	54.6 ± 0.7		53.2 ± 0.8	61.1 ± 0.4	60.7 ± 0.9
ε_{21}	138.5 ± 0.5		138.9 ± 0.9	140.5 ± 0.5	139.4 ± 0.9
$U_{abs} \cdot 10^3$	7.43		—	5.44	—
$U_{rel} \cdot 10^3$	—		9.18	—	6.93
σ(fel[2])					0.017

urements of ε_{11}, and the results come out with large deviations. Obviously it was a good idea to determine ε_{11} separately.

Ahrland's measurements on $SCN^- - UO_2^{2+}$ equilibria (Table 6) seem to fix β_1 well whereas β_2 and β_3 are more uncertain as remarked already by Ahrland. In this and other cases we have been pleasantly surprised by the good fit (relative standard deviation ≈0.005) that can be obtained with spectrophotometric data of high precision.

In Ahrland's studies of $Cl^- - UO_2^{2+}$ (Table 7) only three solutions were used. The fit is improved, not unexpectedly, if a second species is added to the complex UO_2Cl^+. If three species are assumed, it would be possible to get an exact agreement ($U = 0$) with any set of species and equilibrium constants. We give the "best" values for the (1,1) complex alone, and for the combination of the (1,1) and (2,1) species.

Fronaeus' data for $SO_4^{2-} - Cu^{2+}$ (Table 9) allow an estimate of β_{11} for the formation of the (1,1) complex $= CuSO_4$. We have tried to add the mononuclear (2,1) and (3,1), and the binuclear (2,2) and (1,2), using STYRE (part 7). A certain improvement was sometimes found but with the rejection factor F_σ we chose, $F_\sigma = 1.0$, the improvement was not significant for the relative definitions of the error. With absolute errors in E the mononuclear species passed the significance limit, with absolute errors in ε_B the (2,2) species. The results are given in the table, but we do not think the present data

Table 9. Complex formation $SO_4^{2-}(A) - Cu^{2+}(B)$, data of Fronaeus 1948, p. 116. One wavelength (260 nm), 30 solutions, both E values and ε_B values treated.

	Author's β values			
	abs	rel	abs. errors	rel. errors
β_1 from E	5	5	4.48 ± 0.13	4.14 ± 0.14
from ε_B			4.24 ± 0.21	4.14 ± 0.14
ε_{01} from E	1.6 ± 0.2	1.9 ± 0.2	2.3 ± 0.2	2.9 ± 0.2
from ε_B	0.4 ± 0.6	1.9 ± 0.2	2.6 ± 0.5	2.9 ± 0.2
ε_{11} from E	198.0 ± 0.7	195.8 ± 1.2	209.1 ± 0.6	217.0 ± 0.9
from ε_B	199.7 ± 1.1	195.8 ± 1.2	214.5 ± 1.0	216.9 ± 0.9
U_{abs} from E	$7.00 \cdot 10^{-3}$	—	$4.38 \cdot 10^{-3}$	—
from ε_B	62.9	—	44.13	—
U_{rel} from E	—	$15.11 \cdot 10^{-3}$	—	$6.73 \cdot 10^{-3}$
from ε_B	—	$15.12 \cdot 10^{-3}$	—	$6.78 \cdot 10^{-3}$
$\sigma(fel[2])$				0.016

Attempts were made to add more species. With relative errors and the rejection factor $F_\sigma = 1.0$, none of the mono- and binuclear species tried (2,1), (3,1), (1,2) and (2,2) gave a significant improvement.

With absolute errors, some improvement was found,
from ε_B : $\beta_1 = 3.99 \pm 0.26$, $\beta_{22} = 131 \pm 91$, $U = 39.85$ (from 44.13)
from E : $\beta_1 = 3.72 \pm 0.23$, $\beta_2 = 1.22 \pm 0.33$, $U = 3.42 \cdot 10^{-3}$ (from $4.38 \cdot 10^{-3}$)
$\beta_1 = 3.38 \pm 0.38$, $\beta_2 = 1.26 \pm 0.97$, $\beta_3 = 2.19 \pm 1.05$, $U = 2.96 \cdot 10^{-3}$;
β_{22} comes out as 50 ± 52

encourage any conclusion beyond the value for β_1 (and this is what also Fronaeus gave).

At any rate, it would seem to us that the availability of a method that can treat spectrophotometric data, even with quite complicated models, would be an incentive for precise measurements on various complex-forming systems.

We might add that the calculations are quite fast: a few minutes for each of the systems mentioned.

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