MONTE CARLO STUDY OF ERROR PROPAGATION IN THE POTENTIOMETRIC DETERMINATION OF FORMATION CONSTANTS: RESIDUAL ANALYSIS

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ABSTRACT

Realistic estimates of standard deviations of the formation constants of metal ion complexes calculated from potentiometric titrations can be quantified by a Monte Carlo-based technique from estimates of the experimental errors in titration parameters. This Monte Carlo analysis has also potential implications for model selection.

A Matlab® programme is presented to quantify the statistical uncertainty on the optimized stability constants in complex models. The programme consists of a data generation part and a refinement part. The refinement algorithm uses the nonlinear least squares method to minimize the sum of weighted squared differences between the experimental and calculated electrode potentials. It is demonstrated from an analysis of simulated and experimental data of Ag(I)-diamine complex equilibria in certain cases the risk of accepting a false model is real! Residual plots show that the χ^2 test is the least convincing and most controversial criterion for model selection. Some new criteria to increase the reliability of potentiometric data are formulated.

Keywords: Stability constants; Potentiometry; Complex equilibria; Chemometrics; Model selection; Modelling

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INTRODUCTION

The calculation of formation constants of metal complexes is an important and active area of modern solution chemistry. A crucial factor in equilibrium studies is the design of the chemical model. In order to identify the "best" model, a set of hypotheses that describe a number of complexes and their stoichiometric coefficients should be formulated. The corresponding stability constants may be evaluated either approximately by different graphical methods [1] or more precisely by a variety of regression techniques [2-5]. The influence of the computational strategy used on the reliability of stability constants is also discussed in the literature [6-7].

Recently, most of the work related to quantifying the accuracy of equilibrium models and their corresponding stability constants is based on chemometrical methods [8-12]. However, a well-founded statistical error analysis is lacking in the majority of these optimisation programs. The present work shows a detailed error analysis in the determination of stability constants that is rarely done. Better assessment of experimental and systematic errors and structural perturbations in the model makes it possible to select the set of parameters which, when optimized, yields the result with greatest probable accuracy. Moreover, this approach accounts for many discrepancies in the formation constant literature.

EXPERIMENTAL

Materials

Most of the reagents used were commercially available. Detailed information on all products and particularly on the preparation of the diamines used in the complexometric Ag(I)-diamine titrations (1,4-Diaminobutane and 1,5-Diaminopentane) has been published elsewhere [13].

Automated Apparatus

Potentiometric data were obtained with a Radiometer pHM 84 (resolution 0.1mV), equipped with a glass (Ingold pH0-14 HA265-S7/120) and a reference (Ingold Argental 363-S7) electrode couple. Combined pH/pAg measurements were performed with a Radiometer pHM 84 (pH) and a Knick pH Meter 764 multicalimatic (pAg) (resolution 0.1mV). The following electrode couples were used : a glass (Ingold pH 0-14 HA265-S7/120) in combination with a reference (Ingold Argental 363-S7) electrode and the reference electrode (Ingold Argental 363-S7) combined with a Ag/Ag_2S (Orion 94-16) electrode. The design of the fully automated experimental set-up for both pH and combined pH/pAg measurements has been presented in the literature [14-17].

Titrations

The specific procedures used for the potentiometric acid-base titrations as well as the Ag(I)-diamine complexometric titrations have been described elsewhere [13].

RESULTS AND DISCUSSION

The simulated titration curves for two artificial systems ‘sys1’ and ‘sys2’ (table 1) made of 80 points each were generated using the data generation part of the MatLab® program [18] of which the algorithm is based on the program ‘EQUIL’, a general computational method for the calculation of solution equilibria [19]. The curves were subjected to the same analysis as the experimental data with the use of the refinement part of the MatLab® program suite [18]. The core of the refinement algorithm is a Gauss-Newton minimization of a sum of weighted squared residuals in electrode potential based on implicit differentiation in accordance with the program SUPERQUAD [5,20-23]. It is demonstrated

in recent publications dealing with the analysis of experimental Cu(II)- and Ag(I)-diamine complexation data using SUPERQUAD that two main problems arise when interpreting the results [17,24]: on the one hand the residuals in pH or electrode potential do not show a normal distribution character or tend to deviate systematically in certain regions of the titration curve. On the other hand the calculated standard deviations on the optimized constants are not realistic. The literature reports on a qualitative study handling the reliability of computer analysis by means of deviations in the model [7]. Our aim is analysing quantitatively the effects of experimental and structural errors in the chemical model to formulate some new criteria to increase the reliability of potentiometric data.

Quantifying accuracy by means of experimental errors: analysis of 'sys1' and 'sys2'

In order to quantify the effects of systematic and other experimental errors on the optimized stability constants and to make the curves more realistic, each titration point was biased by computer generated random errors with gaussian distribution. As the introduced perturbations are of the same order as in a real experiment, the results can be used for verification of reliabilty of results from analysis of real system data.

The effects of noise in the following titration parameters on the optimized constants have been evaluated :

- Perturbations in pH or electrode potential
- Perturbations in added volume of titrant
- Perturbations in total concentration of metal, ligand and proton
- Perturbations in total initial volume

Considering the vast number of various possible hypotheses and number of simulated experiments for all relevant titration parameters, we have compiled our figures to include

some representative examples (e.g. analysis of the artificial model ‘sys1’ and ‘sys2’ related to perturbations in pH or electrode potential).

The free concentration pH_{ideal} has been generated using the data generation part of the MatLab® program [18]. Errors in pH_{ideal} were modellated by means of a computer generated random variable ε_i with gaussion distribution:

$$pH_{error}(i) = pH_{ideal}(i) + \varepsilon_i \qquad \varepsilon_i \sim N(0, \sigma^2) \tag{1}$$

where i represents the titration point and σ^2 is constant over the whole titration area. Moreover, we assume that there is no correlation between the errors in different titration points. In the example presented in figures 1a. and 1b., the mean value of different stability constants β in the trail-models ‘sys1’ and ‘sys2’ is plotted against log σ.

β is defined as the overall formation constant of the following reaction:

$$pM + qL + rH \rightleftharpoons M_pL_qH_r \qquad \beta_{pqr} = [M_pL_qH_r] / [M]^p [L]^q [H]^r$$

A regression analysis of the standard error (s.e.) on the individual optimized parameters as a function of the perturbation in pH (σ) illustrates linearity in ‘sys1’ (figure 2a.) but non-linearity in ‘sys2’ (figure 2b.)! Thus, the influence of a perturbation in a titration parameter (e.g. pH) on the precision of the optimized constants strongly depends on the chosen system and the magnitude of the individual constant. These effects probably indicate that the linear error propagation model fails when handling potentiometric data.

Quantifying accuracy by means of structural errors in the model: analysis of ‘sys1’and‘sys2’

The reliability of the computer calculations has been evaluated using structural errors in the models ‘sys1’ and ‘sys2 (table 1).

Extended model of ‘sys1’

The results of different optimization cycli using an extended model of ‘sys1’ - the specie MLH is added - , are summarized in table 2. The corresponding initial values of β_{111} in the

different cycli are: 10^3, 10^5, 10^7, 10^8, 10^9 and 10^{11}. Each simulation counts ten titrations with a constant perturbation in pH of 0.002 units,. This perturbation is present in all the following simulation experiments. The starting values for β_{110}, β_{120}, β_{011} and β_{012} deviate at least 50% from their "real" values. U represents the mean quadratic sum of ten titrations of weighted residuals in pH upon convergence. The mean sample deviation S ($S = (U/n\text{-}m)^{1/2}$), where n is the number of titration points and m is the number of parameters to be optimized) is also tabulated as well as the standard error. Table 2 illustrates that in all cases the parameters β_{110}, β_{120}, β_{011} and β_{012} converge to their "real" value in the model system. This of course is a first indication that the wrong model is accepted! In figure 3 (to the left) the initial value for β_{111} is plotted against the final value of U upon convergence. U seems to be acceptable in the interval $\beta_{111} = [10^5, 10^8]$ (U = 372 for the defined starting model). S should not exceed 3 [13], this means that the maximal acceptable value of U is around 700 (n = 80 and m = 5). On the basis of this criterion, once again, the wrong model is accepted! However, if the initial value of β_{111} is of order 10^9 or higher, the value of U goes up drastically. Thus, we can conclude that by adding a "spurious" and very stable complex no problems are encountered in selecting the right model in this region. Figure 3 (to the right) shows the initial value of β_{111} versus the value of β_{111} upon convergence. It becomes clear from this figure that in case of adding the complex MLH with starting values for β_{111} in the interval $[10^5, 10^7]$, these parameter values fade out upon convergence, which is an indication that the added complex can be discarded or the trial-model is not accepted. In figure 4 (to the left) the concentration of all the components and species in the defined model 'sys1' at equilibrium over the whole titration area is plotted. Figure 4 (to the right) shows the corresponding concentration curve for the extended model (MLH is added). The starting value of β_{111} is taken to be 22, which is the mean value after optimization, starting from an

initial estimation of $\beta_{111} = 10^8$. It can be concluded from this figure that neither the concentration of the individual components (M, L and H) nor the concentration of all formed complexes has been changed fundamentally in the region under study, so that the added complex can be discarded on the basis of non-existence.

Incomplete models of 'sys1'

For the sake of clarity, the evaluation of the model selection procedure for incomplete trial-models of 'sys1' is presented in tabular form (table 3). The values for U and S upon convergence are indicated. The data in table 3 illustrate that the selection of all tested incomplete models leads to unacceptable results: the magnitude of U (S) exceeds the maximal value of 700 (3). Moreover, inspection of the residuals in pH suggests the same conclusion (figures 5a. and 5b., to the left). Some model selection criteria have been stated in a previous paper [13]. To our opinion, verification of two extra characteristics, which are the normal character and the independence of the data in the distribution, is of crucial importance in selecting the "best" model. These characteristics are examined by means of a normal probability plot and a plot of the autocorrelation of residuals. A linear normal probability plot points to a symmetric gaussian distribution, which is shown in figure 5a. (to the right) for the defined model 'sys1' (acceptable value of U (S)=372 (2.21)). On the contrary, for the incomplete model (figure 5b. to the right) - the species ML and ML_2 are missing – the corresponding normal probability plot is not linear. This is a serious indication for not accepting the wrong model. In figure 6 (to the left) the autocorrelation of the residuals is shown for the trial-model 'sys1' and for the incomplete model where ML and ML_2 are missing (figure 6 to the right). The autocorrelation plot gives information about the independence of data: the correlation between the ordered row of residuals and itself after a shift over a certain distance , the "lag", is examined. This "lag" is typical for the structure of

the noise and should be as small as possible. For the incomplete model we can conclude that there are systematic tendencies in the residuals (figure 6 to the right).

Extended model of ‘sys2’

The data in table 4 show, that despite the fact that all parameters converge to acceptable values, the wrong model can be discarded on the basis of a huge value of U and S.

Incomplete model of ‘sys2’

An illustration is provided by the results of the refinement procedure of an incomplete model of the more complicated and unstable trial-model ‘sys2’- the complex ML_2 is missing (table 5). The increased number of degrees in freedom in ‘sys2’ could be expected to make the refinement easier. However, this is not the conclusion in the present analysis. It is seen from table 5 that the magnitude of U is not too high and deviates only a factor 10 in comparison with the trial-model. Verification of residuals seems to be recommended. In figures 7a. and 7b. the residuals in pH are plotted for the whole titration area (80 points) together with their corresponding normal probability plots. Figure 7b. gives evidence for some systematic trends in the residuals of the incomplete model. Indeed, only in the basic region of the titration curve the residuals deviate systematically (the complex ML_2 which is normally detected in the basic region [13] is missing in the model!). The computer calculations cannot compensate for these effects! This is confirmed by a plot of the autocorrelation length (figures 8a. and 8b.), which is small in the case of the starting model ‘sys2’ and rather large for the deviating model.

Figure 9 shows a distribution curve of the trial-model ‘sys2’ (to the left) and the corresponding curve (to the right) for the incomplete model where ML_2 is missing. It is illustrated that the concentration curves for the individual components and the species are

not influenced when a complex is missing in the model, also on this basis the deviating model can be discarded.

Combined model of 'sys2'

Table 6 summarizes the results for the refinement procedure of a combined model of 'sys2' where the complex MLH is missing and ML_2H has been added. Here, some problems arise in selecting the correct model: all parameters converge to an acceptable value and the value of U (S) is realistic! It becomes obvious that the "S-criterion" is not sufficient for model selection . On the other hand examination of the distribution curves (figure 10) and verification of residual plots is absolutely indispensable. It becomes clear from figure 10 (to the right) that the "spurious" complex ML_2H is only present in a minor quantity and does not influence the concentration curves of the individual components and species.

Quantifying accuracy using experimental data of Ag(I)–1,4-diaminobutane complex equilibria

Inspection of residuals in E_{Ag} for the Ag(I)-1,4-diaminobutane model that fits best the experimental data (S = 2.33) [13], shows a linear normal probability plot (figure 11) and a small autocorrelation length (figure 12). This confirms our foregoing conclusions which are of course stated on the basis of "well-known" models. It follows from our experience that in optimizing real systems, the χ^2 criterion is the most controversial and least convincing test for model selection: a large value of χ^2 (> 12.60 indicates systematic trends in the residuals [18]) is neglected if the sample standard deviation S is favourable (<3)!

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REFERENCES

[1] J.F.C. Rossotti, H. Rossotti, The Determination of Stability Constants and Other Equilibrium Constants in Solution, Mc Graw-Hill Book Company, Inc., New York, (1961).

[2] A. Sabatini, A. Vacca, P. Gans, Talanta 21 (1974) 53.

[3] J. Havel, M. Meloun, Talanta 33 (1986) 435.

[4] J. Kostrowicki, A. Liwo, Computers and Chemistry 11 (1987) 195.

[5] P. Gans, Data Fitting in the Chemical Sciences, Wiley, Chichester, (1992).

[6] M. Meloun, V. Centner, Analyst 118 (1993) 1543.

[7] L. Lomozik, Chem. Anal.(Warsaw) 44 (1999) 89.

[8] A. Ravindra Babu, D. Murali Krishna, P. Sambasiva Rao, Talanta 40 (1993) 1873.

[9] R. Garner, J. Yperman, J. Mullens, L.C. Van Poucke, Anal. Chim. Acta 282 (1993) 471.

[10] M. Meloun, V. Centner, Talanta 41 (1994) 99.

[11] J.M. Diaz-Cruz, R. Tavler, B.S. Gravaric, M. Esteban, E. Casassas, Journal of Electroanalytical Chemistry 393 (1995) 7.

[12] A. Braibanti, R. Sambasiva Rao, A. Ravindra Babu, G. Nageswara Rao, Annali di Chimica 85 (1995) 17.

[13] W.J. Guedens, J. Yperman, J. Mullens, L.C. Van Poucke, J. Coord. Chem. 47 (1999) 17.

[14] R. Garner, J. Yperman, J. Mullens, L.C. Van Poucke, Bull. Soc. Chim. Belg. 102 (1993) 3.

[15] R. Garner, J. Yperman, J. Mullens, L.C. Van Poucke, J. Coord. Chem. 30 (1993) 151.

[16] R. Garner, J. Yperman, J. Mullens, L.C. Van Poucke, Inorg. Chim. Acta 224 (1994) 97.

[17] R. Garner, Ph.D. Thesis, L.U.C., Diepenbeek (1993).

[18] W.J. Guedens, Ph.D. Thesis, L.U.C., Diepenbeek (1999).

[19] I. Ting-Po, G.H. Nancollas, Anal. Chem. 44 (1972) 1940.

[20] A. Sabatini, A. Vacca, P. Gans, Coord. Chem. Rev. 120 (1992) 389.

[21] P. Gans, A. Sabatini, A. Vacca, Inorg. Chim. Acta 79 (1983) 219.

[22] P. Gans, A. Sabatini, A. Vacca, J. Chem. Soc. Dalton Trans. (1985) 1195.

[23] P. Gans, Manual SUPERQUAD (1989).

[24] K. Brassinne, Ph. D. Thesis, L.U.C., Diepenbeek (1997).

TABLE 1

Composition and overall formation constants β (log units) characterizing the artificial model systems ‘sys1’ and ‘sys2’. The initial parameters for both systems: C_M = 0.001 mol l^{-1}, C_L = 0.005 mol l^{-1}, C_H = 0.1 mol l^{-1}, titrant concentration C_{KOH} = 0.1 mol l^{-1}. C_M, C_L and C_H respectivily being the initial total concentration of metal, ligand and proton

‘sys1’		‘sys2’	
complex	log β	complex	log β
ML	8	MLH	12
ML_2	14	ML_2	6
HL	9	ML	3
H_2L	11	HL	10
		H_2L	17
		OH^-	-14

TABLE 2

List of the mean value of the minimization function U (ten titrations), s.e. and the sample standard deviation S (between brackets). The optimized parameters β_{pqr} , upon convergence, of an extended model of 'sys1' are summarized. The complex MLH is added to the system with the following initial estimations of β_{111}: 10^3, 10^5, 10^7, 10^8, 10^9, 10^{11}

β_{111}	$\overline{U} \pm s.e.$ ($\overline{S}$)	$\overline{\beta_{110}} \pm s.e.$	$\overline{\beta_{120}} \pm s.e.$	$\overline{\beta_{011}} \pm s.e.$	$\overline{\beta_{012}} \pm s.e.$	$\overline{\beta_{111}} \pm s.e.$
10^3	$2.131010^3 \pm 3.990610^2$ (5.33)	$1.001410^8 \pm 1.395810^5$	$1.001810^{14} \pm 1.260910^{11}$	$1.000310^9 \pm 1.590810^5$	$1.000410^{11} \pm 2.724010^7$	$3.054710^1 \pm 4.7982$
10^5	$4.579510^2 \pm 5.3519$ (2.47)	$1.009810^8 \pm 2.986110^5$	$1.008810^{14} \pm 3.010910^{11}$	$1.000910^9 \pm 5.441310^5$	$1.002010^{11} \pm 6.072610^7$	$8.009910^{-3} \pm 1.185810^{-4}$
10^7	$4.895710^2 \pm 1.8292$ (2.55)	$1.010010^8 \pm 2.871410^5$	$1.010210^{14} \pm 2.698710^{11}$	$1.000410^9 \pm 1.627810^5$	$1.002410^{11} \pm 5.811110^7$	$1.567710^{-2} \pm 5.188810^{-4}$
10^8	$6.332810^2 \pm 9.9028$ (2.90)	$1.004610^8 \pm 1.670710^5$	$1.001210^{14} \pm 7.079810^{10}$	$1.004210^9 \pm 1.609710^6$	$1.006010^{11} \pm 2.560010^8$	$2.231510^1 \pm 1.7873$
10^9	$7.527710^3 \pm 9.399410^1$ (10.02)	$1.006110^8 \pm 2.046410^5$	$1.004410^{14} \pm 1.917710^{11}$	$1.003810^9 \pm 2.301310^6$	$1.003410^{11} \pm 2.315610^8$	$2.870810^3 \pm 1.498710^2$
10^{11}	$3.184710^4 \pm 7.688210^2$ (20.61)	$1.003410^8 \pm 1.499910^5$	$1.005410^{14} \pm 2.569110^{11}$	$1.003210^9 \pm 1.841310^6$	$1.000910^{11} \pm 4.964110^7$	$5.226910^8 \pm 9.269210^6$

TABLE 3

Results for the optimized overall formation constants of some incomplete models of the model system ‘sys1’. The “real” parameter values are indicated between brackets. The U-statistic and (sample standard deviation S) are also indicated

	Model	$\log \beta_{pqr}$ initial value	$\log \beta_{pqr}$ optimized value	U ($x10^9$) S ($x10^3$) (convergence)
1)	ML	8.17609 (8)	8.45327	5.35 8.23
2)	ML	8.17609 (8)	7.77895	2.84
	ML_2	13.69897 (14)	-5.87324	6.03
3)	HL	9.17609 (9)	9.11257	2.79
	H_2L	10.69897 (11)	-3.27768	5.98
4)	ML_2	13.69897 (14)	13.60352	0.083
	HL	9.17609 (9)	7.27167	1.04
	H_2L	10.69897 (11)	10.47695	
5)	ML	8.17609 (8)	7.56829	0.035
	HL	9.17609 (9)	7.27180	0.68
	H_2L	10.69897 (11)	10.32212	

TABLE 4

Results of the optimisation procedure of an extended model of ‘sys2’ - the complex ML_2H has been added . The “real” parameter values are indicated between brackets. The U and (S)-statistics are also mentioned

Model	log β_{pqr} starting value	log β_{pqr} optimized value	$Ux10^7$ ($Sx10^3$) upon convergence
MLH	12.17609 (12)	12.17615	8.28 (1.07)
ML_2	5.77085 (6)	5.77084	
ML	3.17609 (3)	3.17612	
HL	9.69897 (10)	9.69900	
H_2L	17.15299 (17)	17.15226	
OH^-	-14.22915 (-14)	-14.22914	
ML_2H	5.17609	7.95654	

TABLE 5

Results of the refinement procedure of an incomplete model of 'sys2' – ML_2 is missing. The "real" parameter values are between brackets. U- and S- statistics are also mentioned

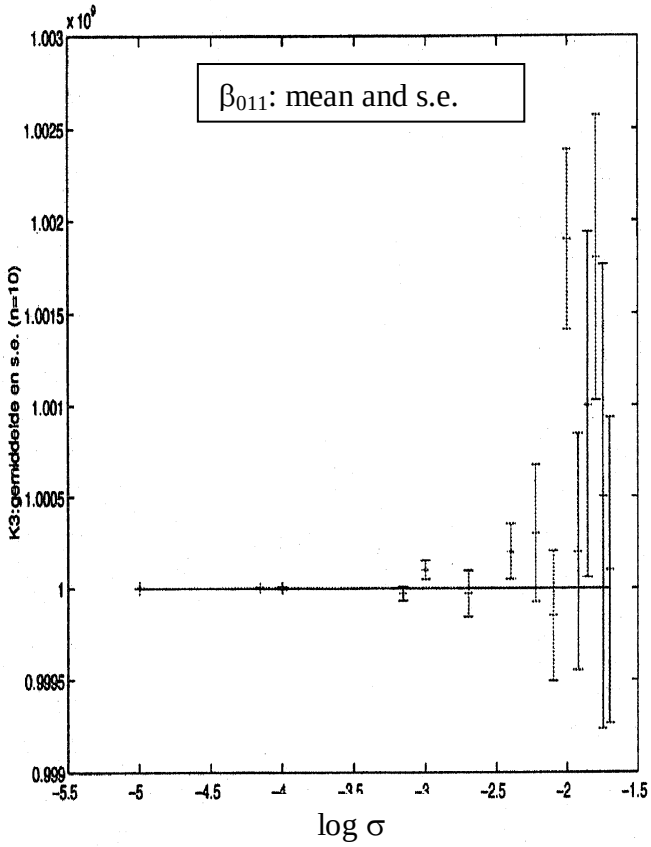
Model	log β_{pqr} initial value	log β_{pqr} optimized value	$Ux10^3$ (S) upon convergence
MLH	12.17609 (12)	11.98612	6.09 (9.01)
ML	3.17609 (3)	2.65716	
HL	9.69897 (10)	9.80500	
H_2L	17.15299 (17)	16.82029	
OH^-	-14.22915 (-14)	-14.09657	

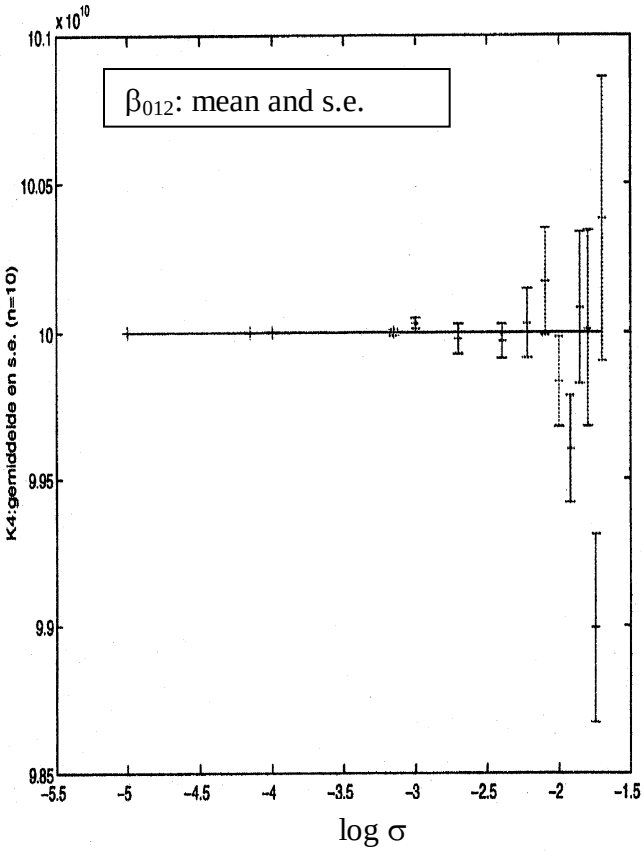
TABLE 6

List of optimized constants and U (S)-statistics in the incomplete model of ‘sys2 – the complex MLH is missing and ML_2H has been added to the model. The “real” parameter values are between brackets.

model	log β_{pqr} initial value	log β_{pqr} optimized value	U x 10^2 (S) upon convergence
ML_2	5.77085 (6)	6.03878	1.64 (1.49)
ML	3.17609 (3)	1.76893	
HL	9.69897 (10)	10.02018	
H_2L	17.15229 (17)	16.98589	
OH^-	-14.22915 (-14)	-13.99346	
ML_2H	5.17609	15.12163	

Figure 1a.


x 10^9
1.003
1.0025
1.002
1.0015
1.001
1.0005
1
0.9995
0.999
K3:gemiddelde en s.e. (n=10)
β011: mean and s.e.
-5.5
-5
-4.5
-4
-3.5
-3
-2.5
-2
-1.5
log σ


x 10^10
10.1
10.05
10
9.95
9.9
9.85
K4:gemiddelde en s.e. (n=10)
β012: mean and s.e.
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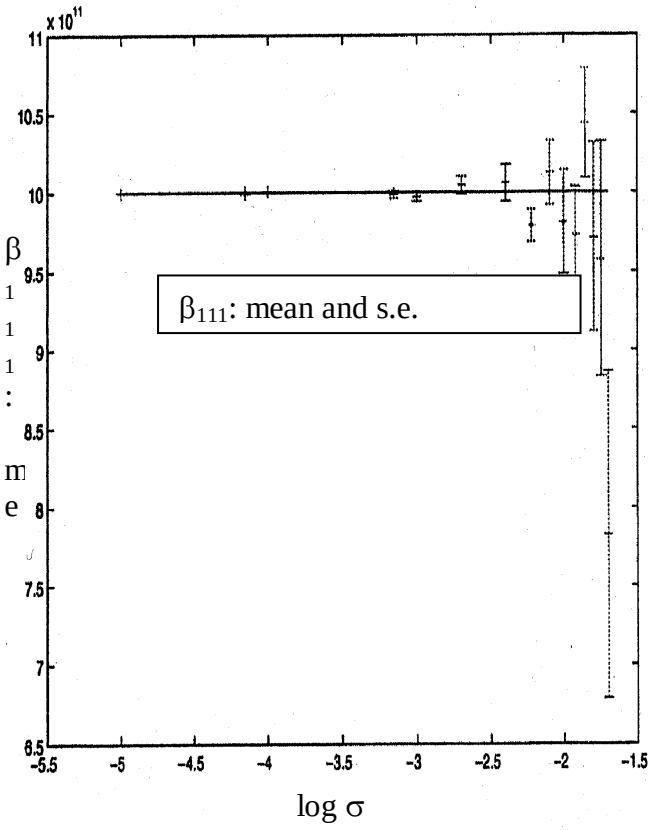
-5
-4.5
-4
-3.5
-3
-2.5
-2
-1.5
log σ

Figure 1b.



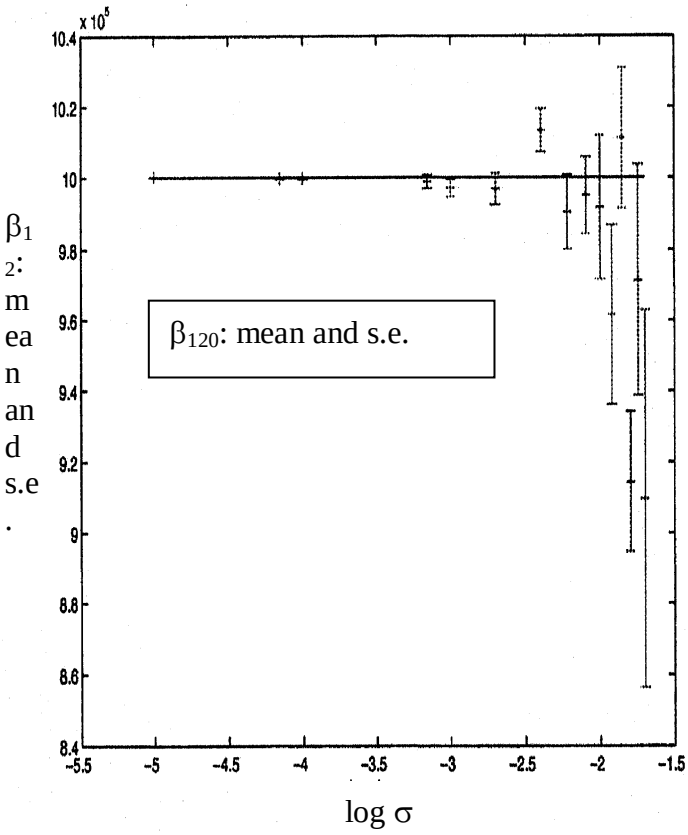


Figure 2a.

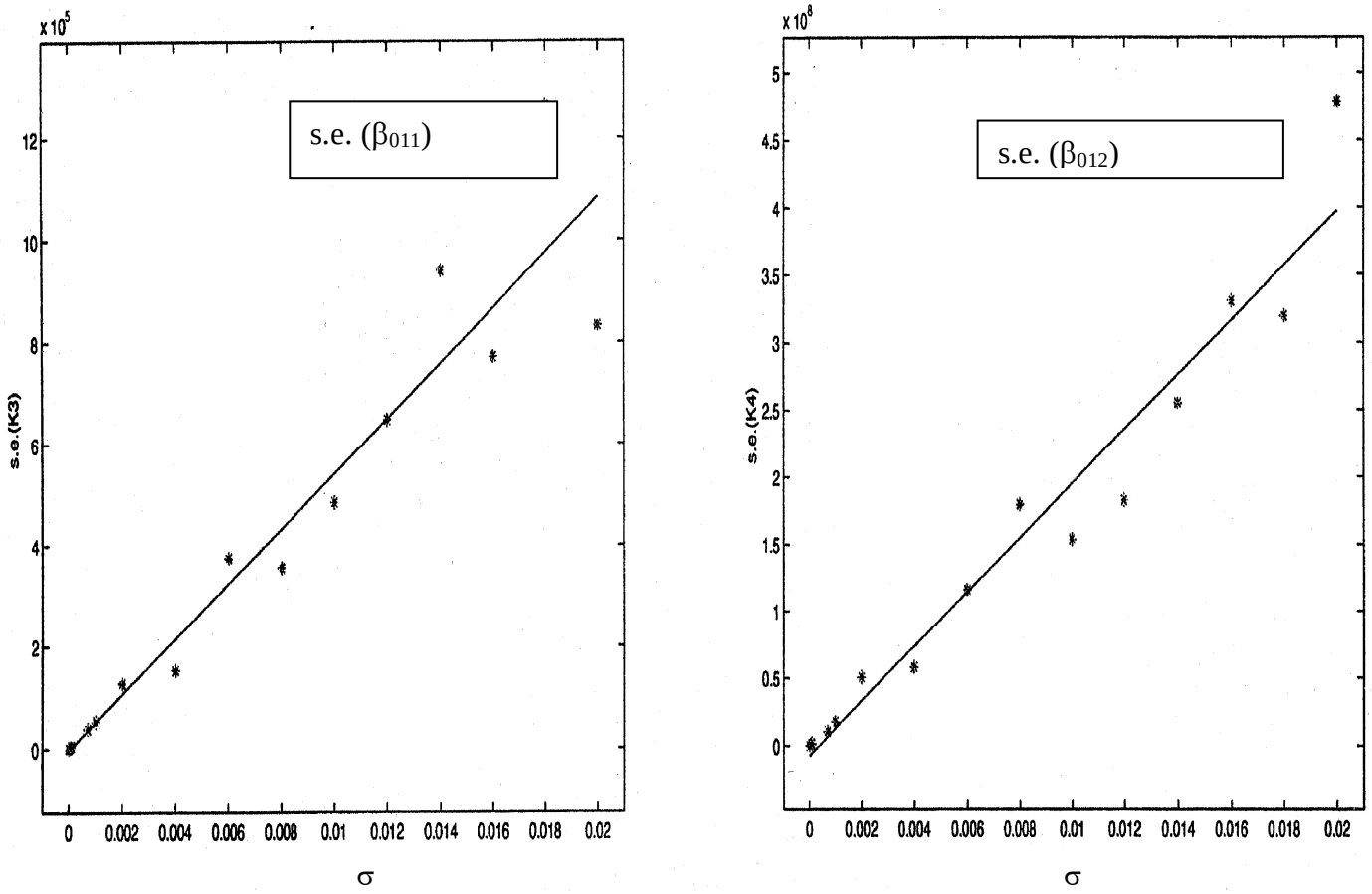

x 10^5
s.e. (β011)
s.e.(K3)
12
10
8
6
4
2
0
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018
0.02
σ
x 10^8
s.e. (β012)
s.e.(K4)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
σ

Figure 2b.

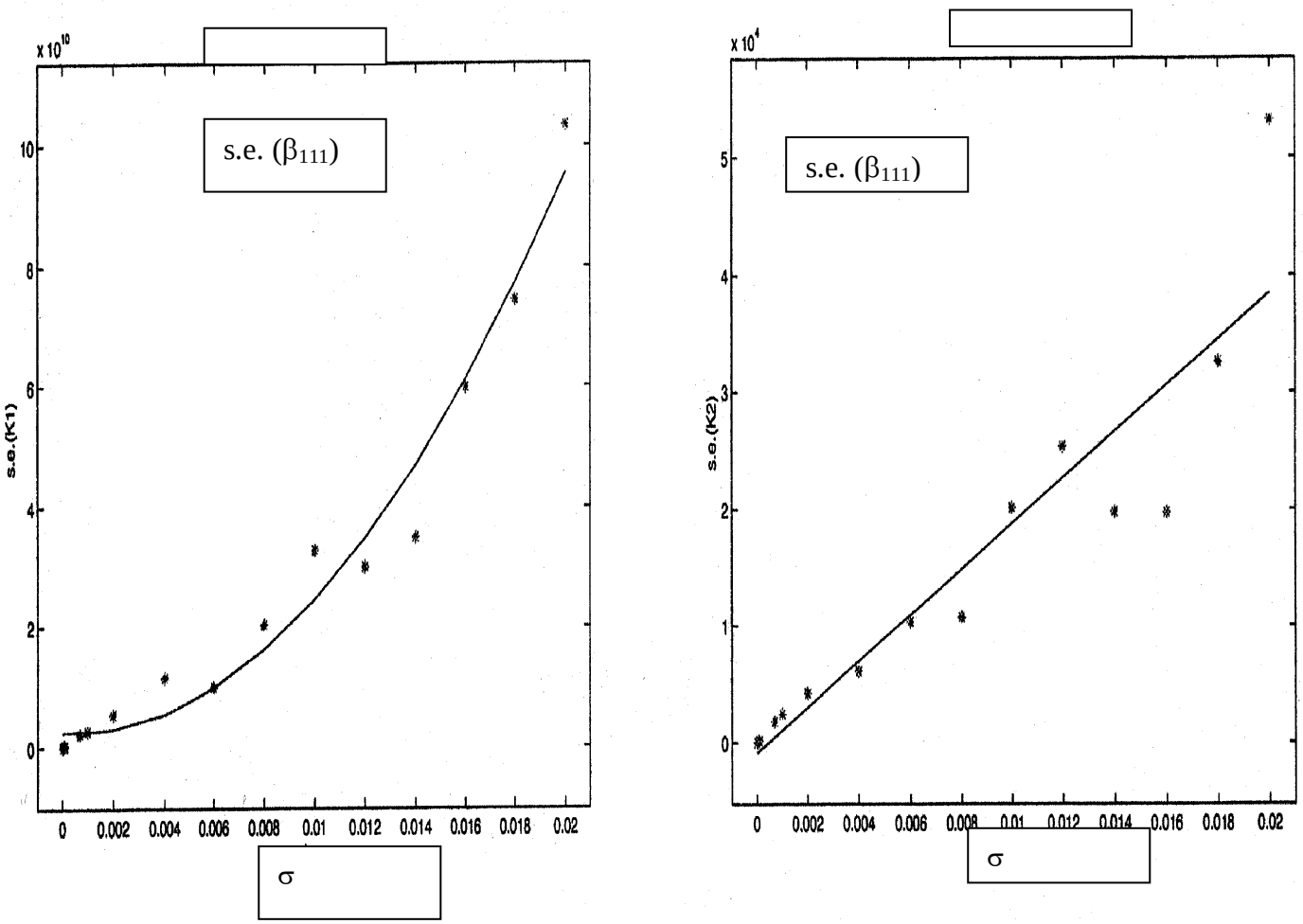

x 10^10
s.e. (β111)
s.e.(K1)
0
2
4
6
8
10
0 0.002 0.004 0.006 0.008 0.01 0.012 0.014 0.016 0.018 0.02
σ
x 10^4
s.e. (β111)
s.e.(K2)
0
1
2
3
4
5
0 0.002 0.004 0.006 0.008 0.01 0.012 0.014 0.016 0.018 0.02
σ

Figure 3

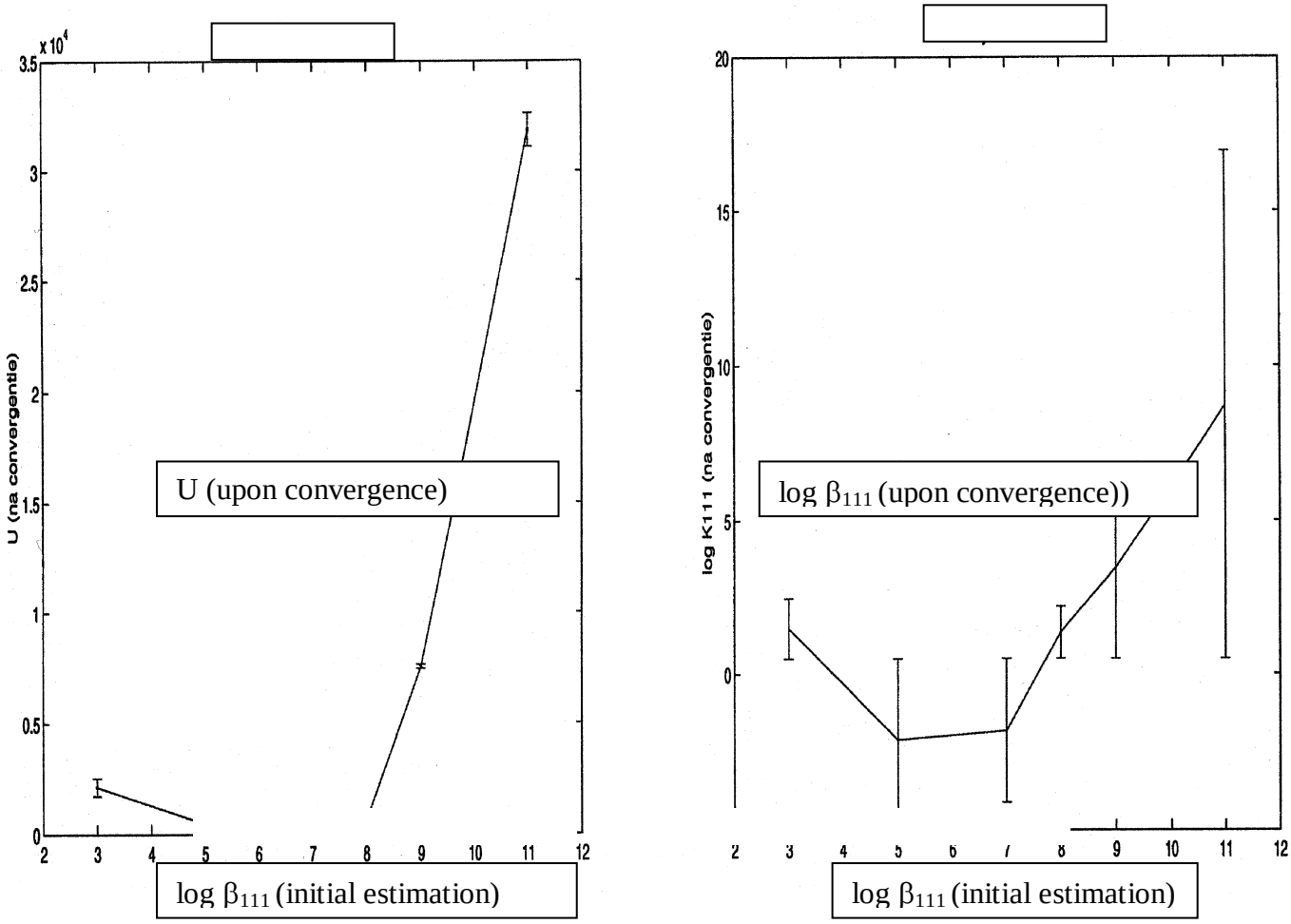

x 10^4
U (na convergentie)
U (upon convergence)
log β111 (initial estimation)
log K111 (na convergentie)
log β111 (upon convergence))
log β111 (initial estimation)

Figure 4

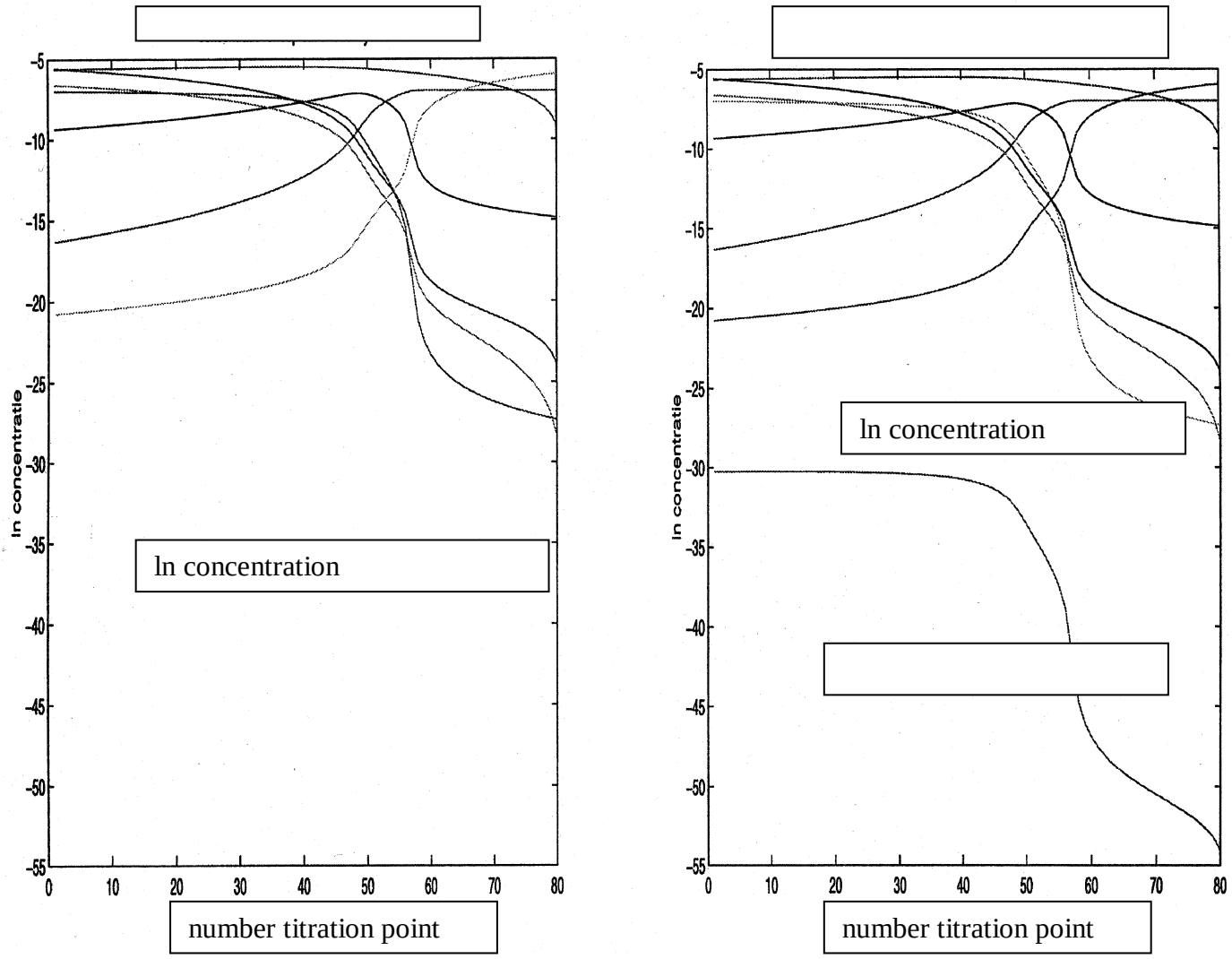
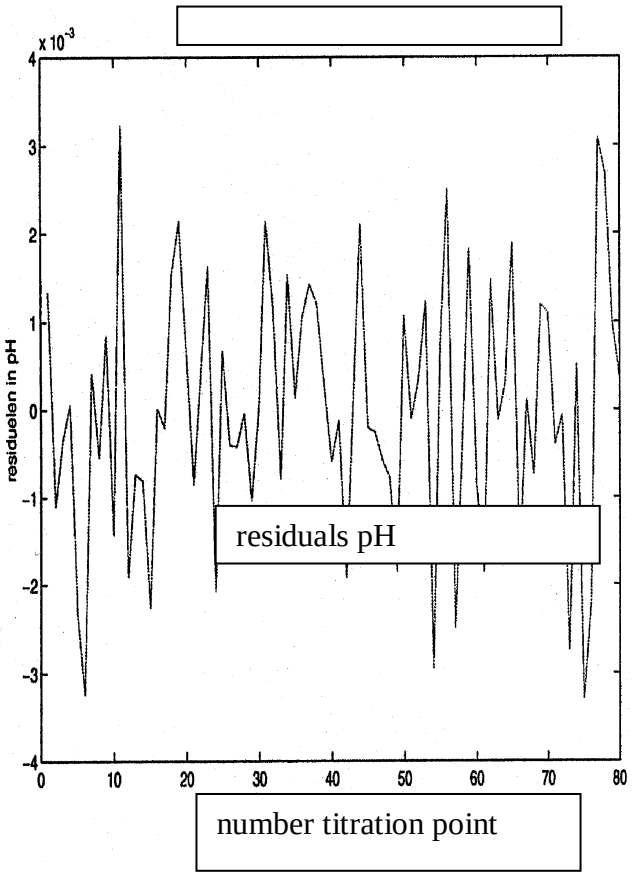

ln concentratie
ln concentration
number titration point
ln concentratie
ln concentration
number titration point

Figure 5a.


x 10^-3
residuelen in pH
residuals pH
number titration point

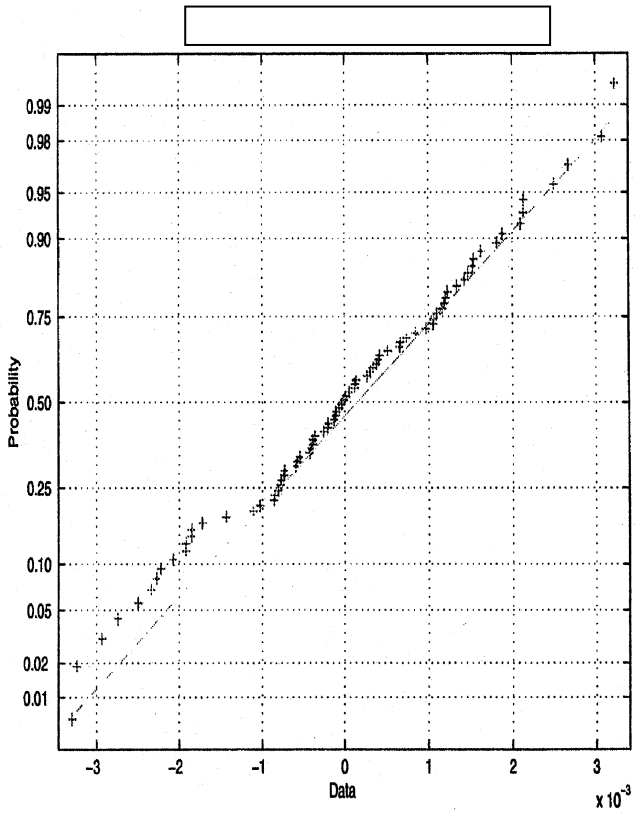
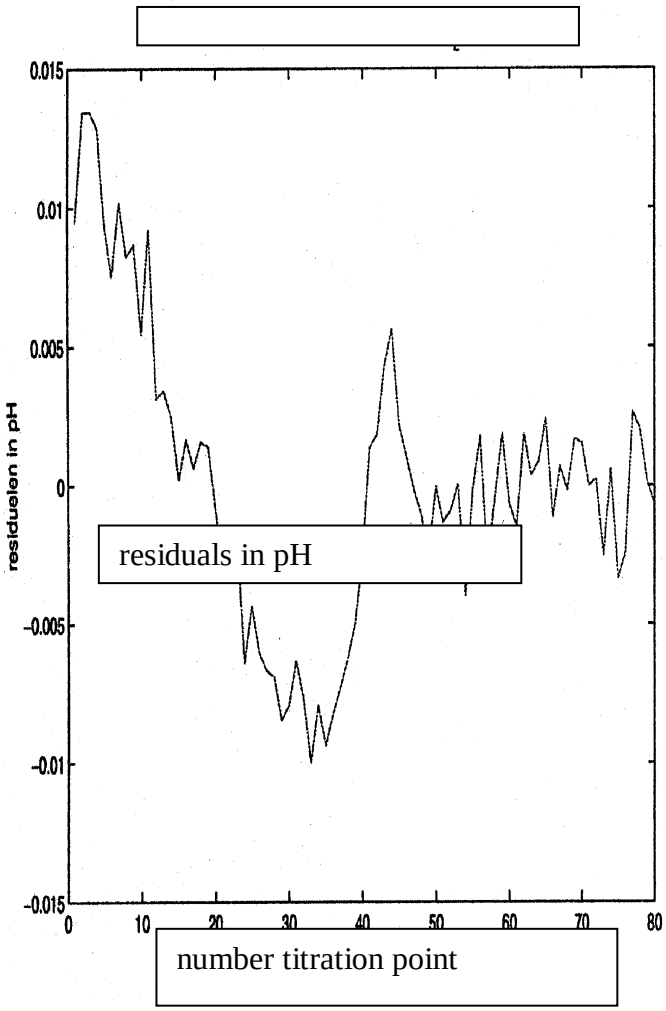

Probability
Data
x 10^-3

Figure 5b.


residuals in pH
number titration point
0.015
0.01
0.005
0
-0.005
-0.01
-0.015
0
10
20
30
40
50
60
70
80

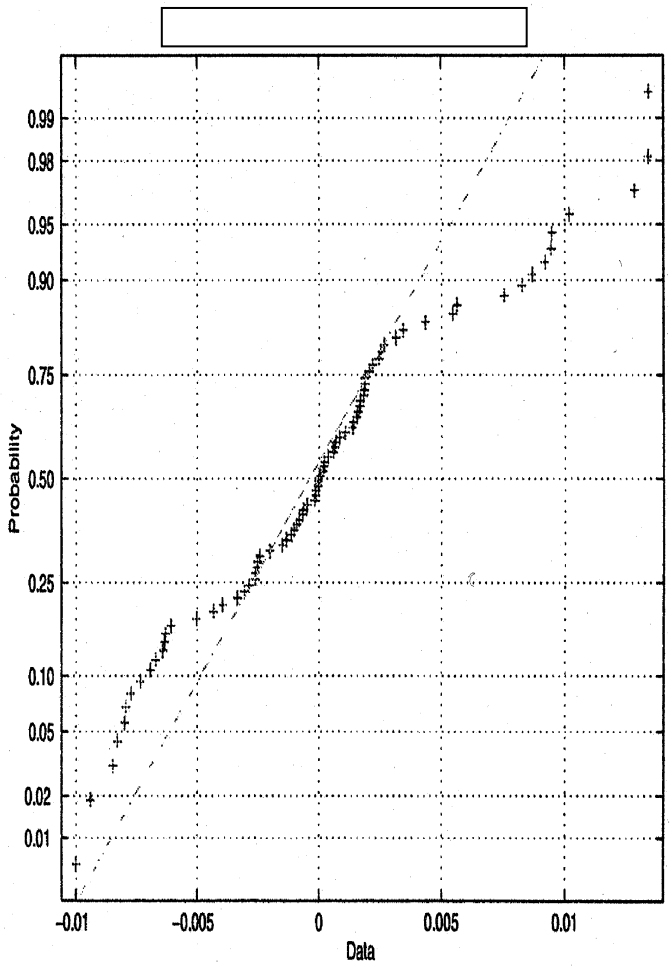

Probability
Data
0.99
0.98
0.95
0.90
0.75
0.50
0.25
0.10
0.05
0.02
0.01
-0.01
-0.005
0
0.005
0.01

Figure 6

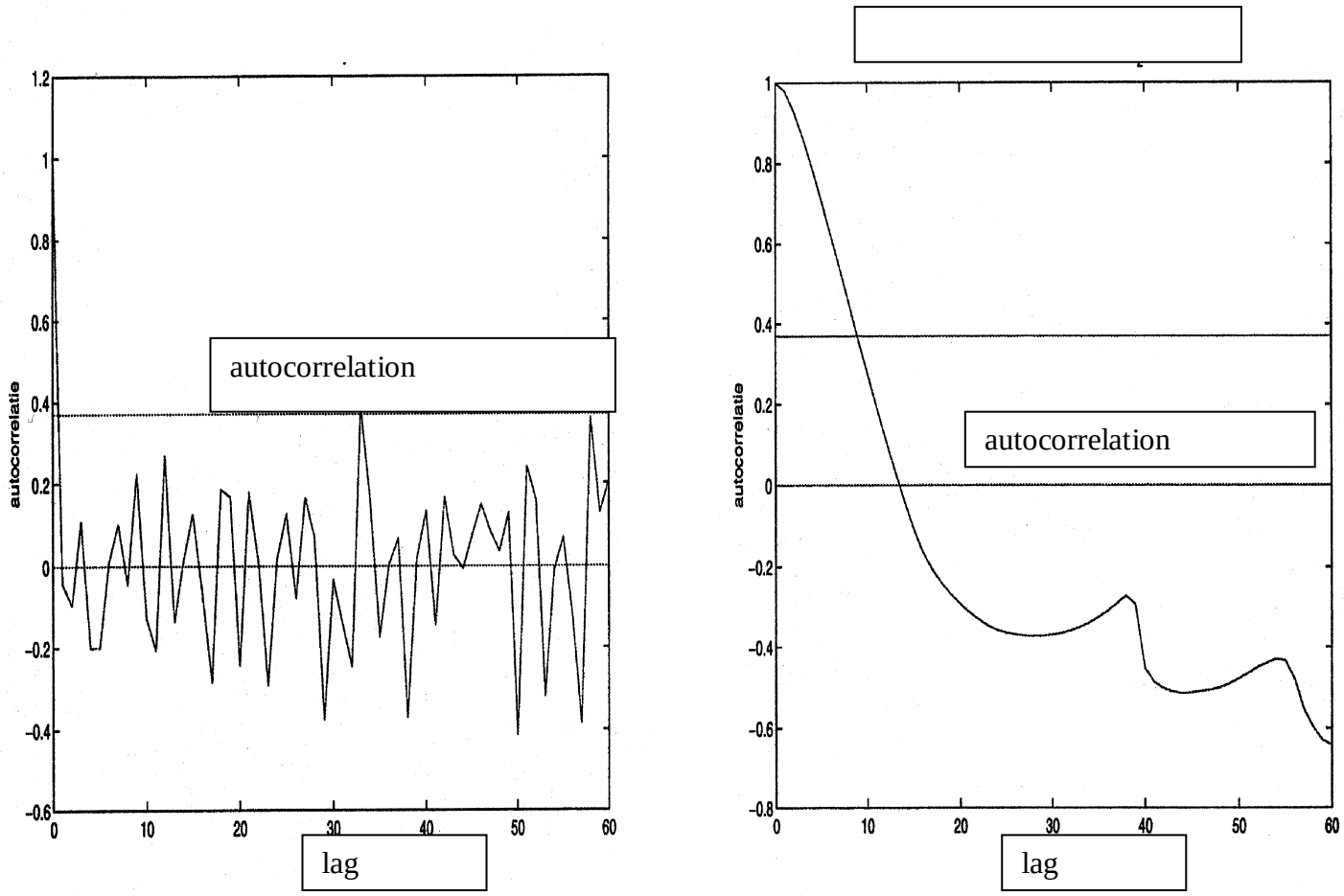
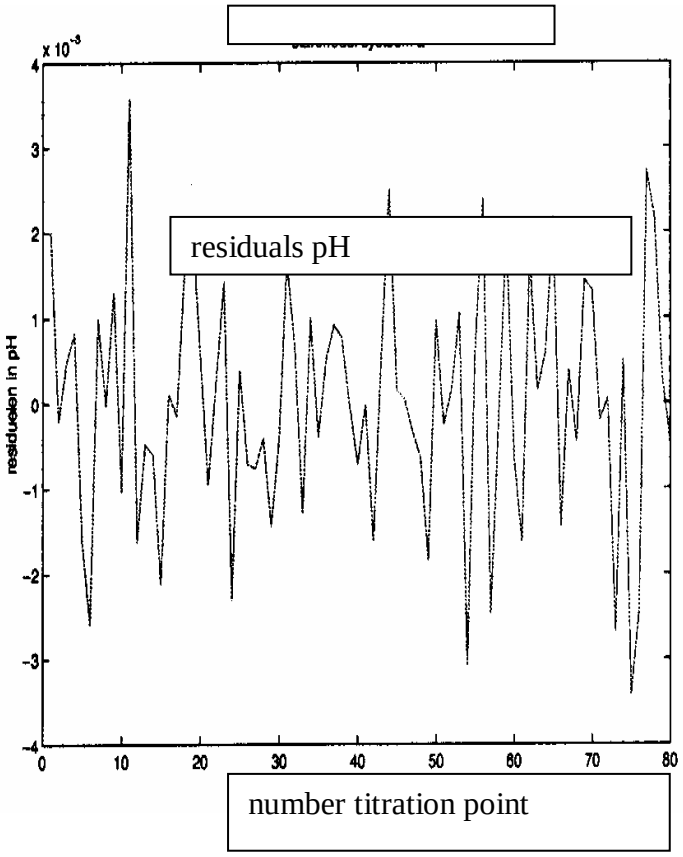

autocorrelatie
autocorrelation
lag
autocorrelatie
autocorrelation
lag

Figure 7a.


residuals pH
residuelen in pH
number titration point

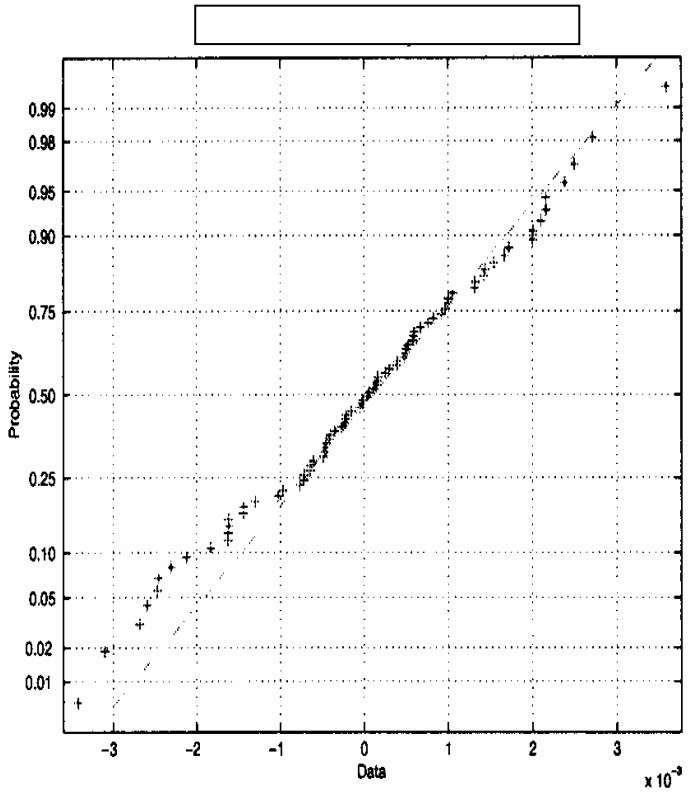
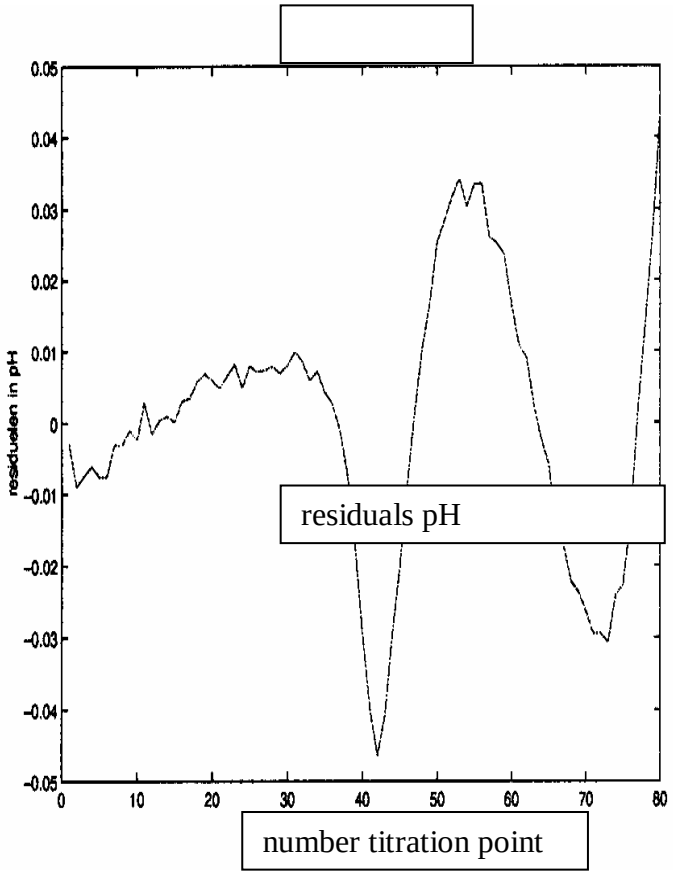

Probability
Data

Figure 7b.


residuelen in pH
residuals pH
number titration point

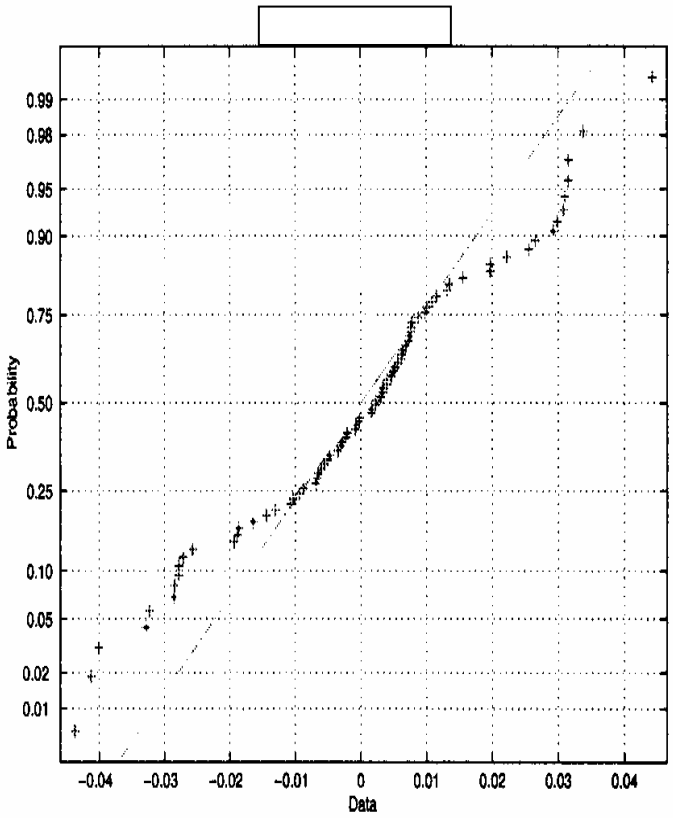

Probability
Data

Figure 8a.

.

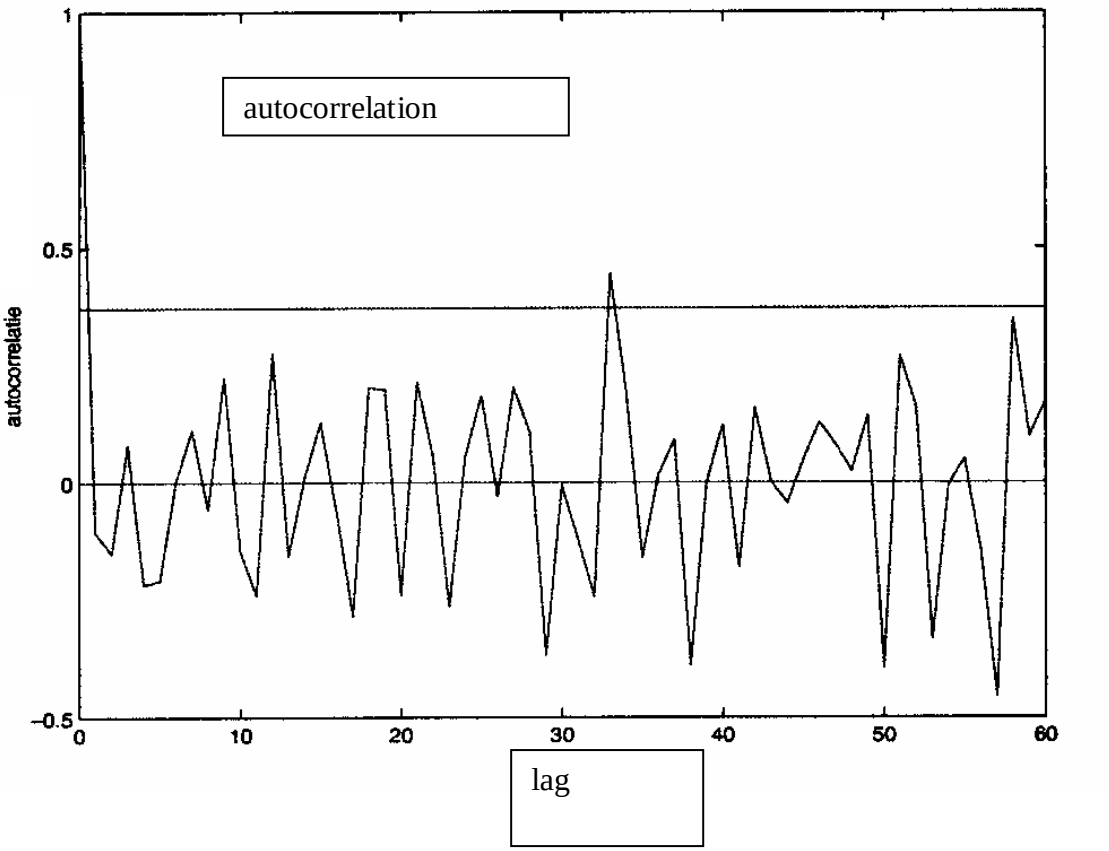

autocorrelation
autocorrelatie
1
0.5
0
−0.5
0
10
20
30
40
50
60
lag

Figure 8b

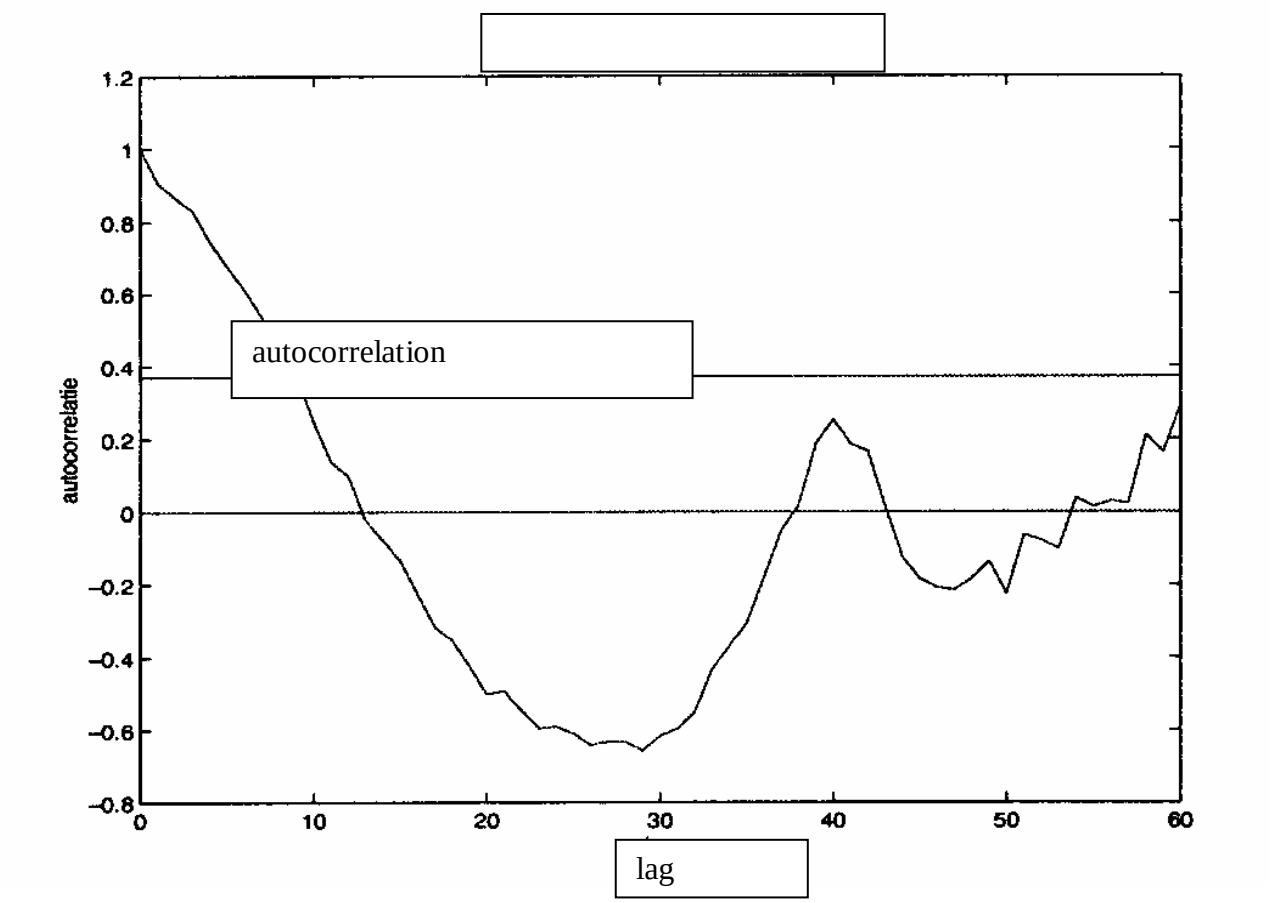
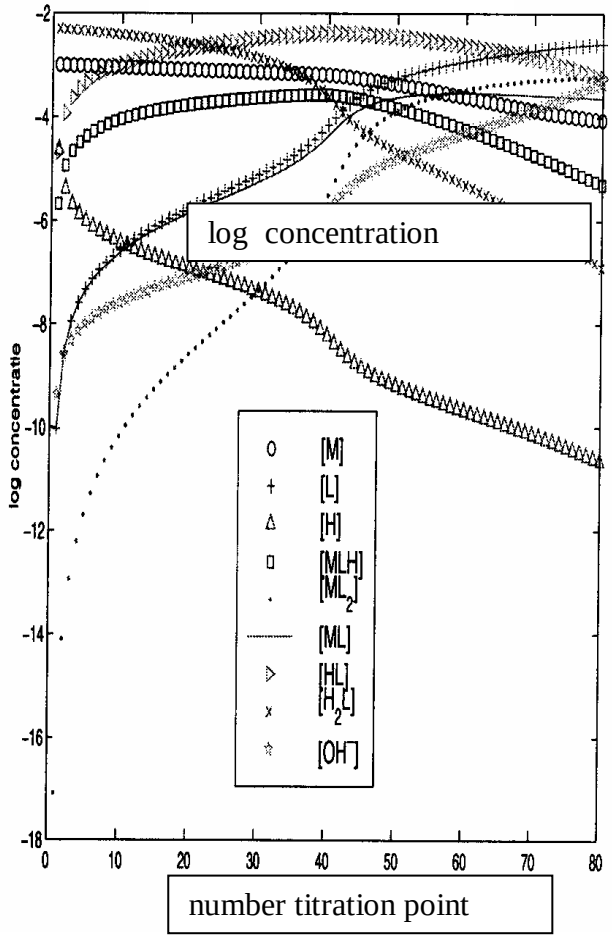

autocorrelation
autocorrelatie
lag
1.2
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.6
−0.8
0
10
20
30
40
50
60

Figure 9


log concentratie
log concentration
[M]
[L]
[H]
[MLH]
[ML2]
[ML]
[HL]
[H2L]
[OH-]
number titration point

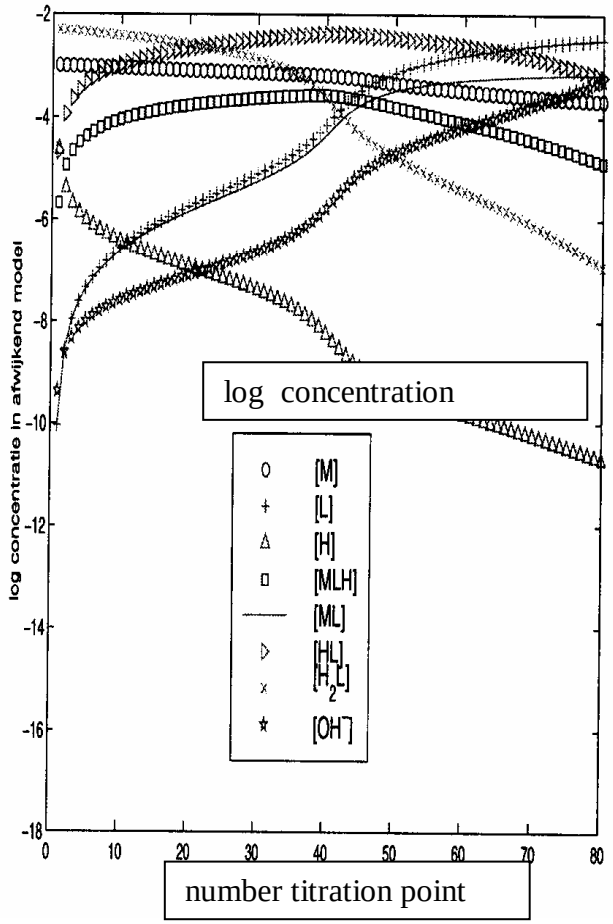

log concentratie in afwijkend model
log concentration
[M]
[L]
[H]
[MLH]
[ML]
[HL]
[H2L]
[OH-]
number titration point

Figure 10

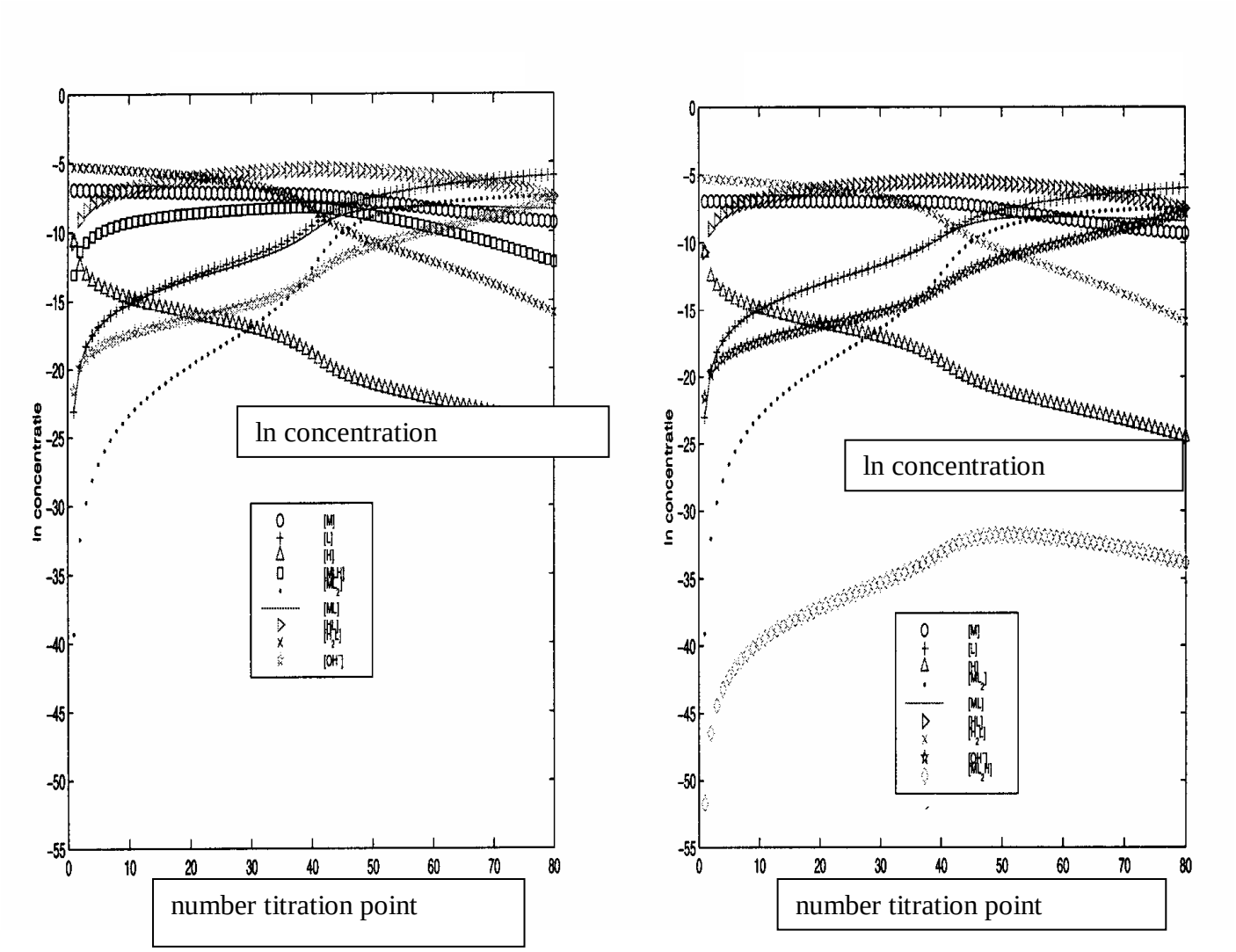

ln concentratie
number titration point
ln concentration
number titration point

Figure 11

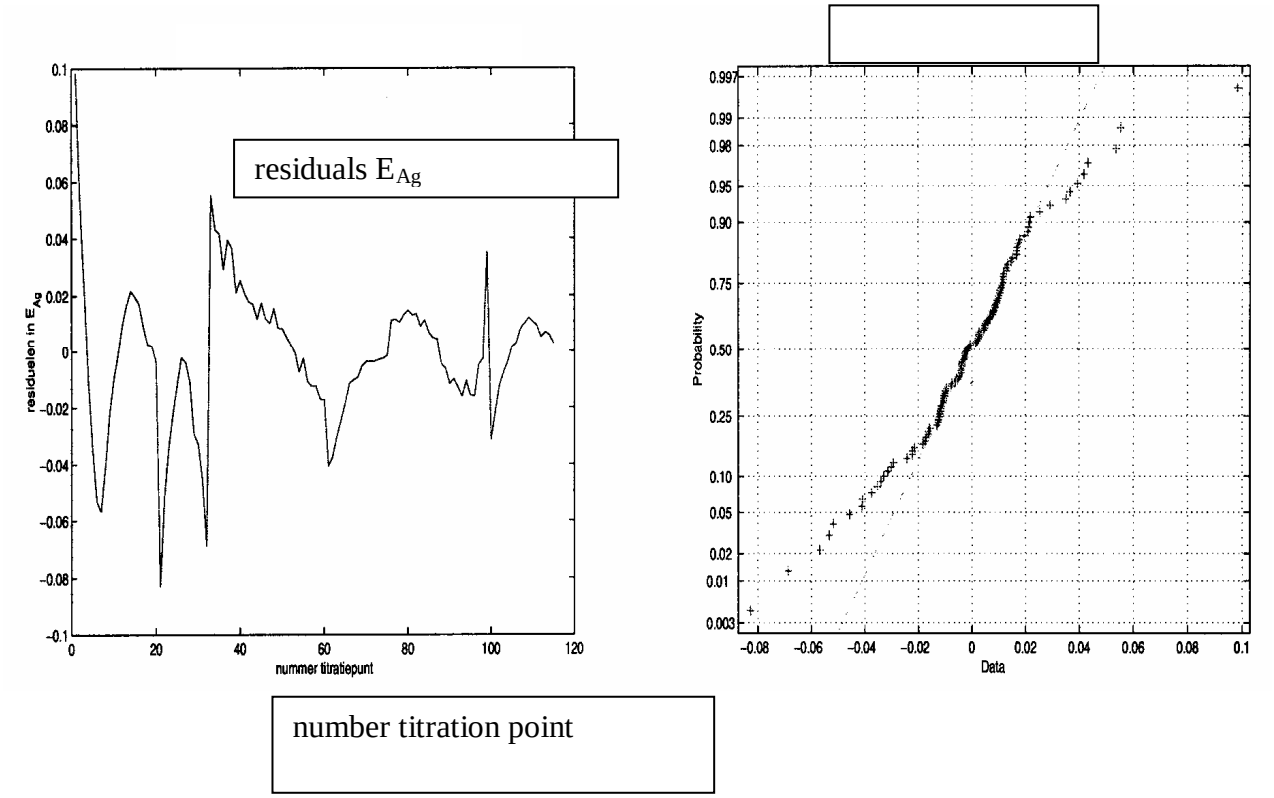
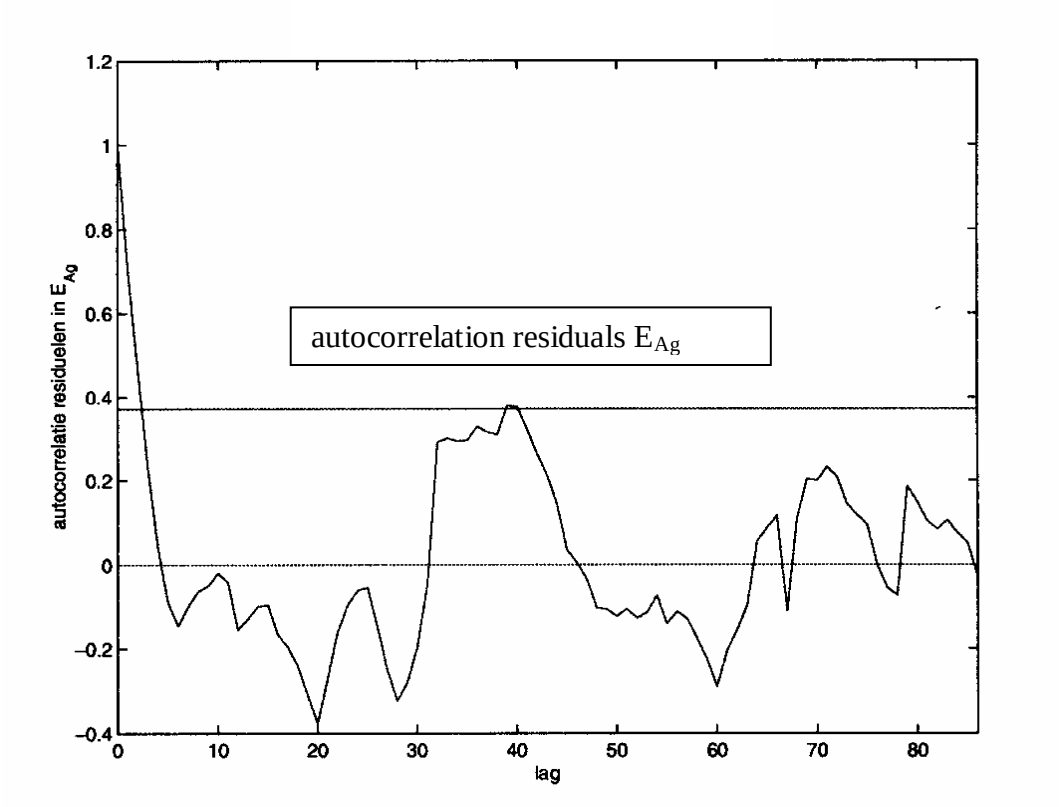

residuals E_{Ag}
residuelen in E_{Ag}
nummer titratiepunt
Probability
Data
number titration point

Figure 12


autocorrelatie residuelen in E_{Ag}
1.2
1
0.8
0.6
0.4
0.2
0
−0.2
−0.4
0
10
20
30
40
50
60
70
80
lag
autocorrelation residuals E_{Ag}
lag

List of descriptive legends of figures

Figure 1a.: Mean β_{011} (left) and mean β_{012} ('sys1') (right) as a function of σ, the magnitude of error in pH (log units). The number of titrations is ten. Error bars equal the standard error on β. The horizontal line represents the "real" β (table 1).

Figure 1b.: Mean β_{111} (left) and mean β_{120} ('sys2') (right) as a function of σ, the magnitude of error in pH (log units). The number of titrations is ten. Error bars equal the standard error on β. The horizontal line represents the "real" β (table 1).

Figure 2a.: S.e. on mean β_{011} (left) and s.e. on mean β_{012} (right) versus σ ('sys1'). The number of Monte Carlo cycles is ten.

Figure 2b.: S.e. on mean β_{111} (left) and s.e. on mean β_{120} (right) versus σ ('sys2'). The number of Monte Carlo cycles is ten.

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Figure 5b.: pH residual plot versus titration point (left) and corresponding normal probability plot for the deviating model of ‘sys1’- ML and ML_2 are missing (right).

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Figure 7a.: pH residual plot versus titration point (left) and corresponding normal probability plot for the trial-model ‘sys2’(right).

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Figure 10: Concentration curve for the individual components and all species in the starting model ‘sys2’(left). Corresponding curve for the model where the complex MLH is missing and ML_2H ($\beta_{121} = 1.5\ 10^5$) has been added to the starting model (right).

Figure 11: E_{Ag} residual plot over the whole titration area for all C_{Ag}/ C_L ratios (left) and corresponding normal probability plot for the experimental system Ag(I)-1,4-diaminobutane (right).

Figure 12: Autocorrelation plot of the E_{Ag} residuals for the experimental system Ag(I)-1,4-diaminobutane.