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The Use of Graph-theoretical Models to Evaluate Two Electroanalytical Methods for Determination of Stability Constants

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Stability constants K_1 and β_2 of copper(II) complexes with alanine and its five *N*-alkylated and *N,N*-dialkylated derivatives were measured by glass electrode potentiometry (GEP) and square wave voltammetry (SWV) and evaluated using graph-theoretical models. Correlations with the connectivity index of the 3rd order, $^3\chi^v$, show that log K_1(GEP) values were better reproduced than log K_1(SWV) values; S.E. = 0.18–0.16 *vs.* 0.29–0.35, respectively. The opposite is true for log β_2 (S.E. = 0.51–0.56 *vs.* 0.39–0.47 for GEP and SWV, respectively). By applying three criteria – 1) difference between GEP and SWV values, 2) difference between SWV and theoretical values, and 3) correlation of experimental error (S.E.$_{exp}$) to the difference between experimental and theoretical values – it was possible to determine three experimental log K_1(SWV) values as problematic. This report demonstrates the value of recently developed graph-theoretical models in planning the experiments and discussing their results.

Keywords
glass electrode potentiometry (GEP)
square wave voltammetry (SWV)
copper(II) chelates
amino acid
stability constant
topological indices

INTRODUCTION

There are many attempts to interpret topological indices,[1–6] but despite smaller or greater success in giving them appropriate physical meaning, there is a little doubt that they provide, both conceptually and computationally, a simple measure of topological, and hence structural similarity. As similar molecules have similar properties, it is not at all surprising that topological indices were successfully correlated to many physicochemical parameters (density, viscosity, boiling temperature, solubility, refractive index, molar heat capacity, standard Gibbs energy of formation, ultrasound velocity),[7–10] and were useful in drug design, *i.e.* QSAR analysis.[11–14]

Based on topological indices we wanted to develop models for the estimation of stability constants that would be accurate and practical. Accurate in the sense that they can predict a value of stability constant with an error commensurable to experimental uncertainty or, at last, to the discrepancy between two or more experimental determinations. Practical in the sense that the theoretical method should not be more demanding than the experimental method for their determination.

We applied our models on various kinds of complexes, *i.e.* copper(II) and nickel(II) chelates with α-amino acids and their *N*-alkylated derivatives,[15–17] diamines and triamines,[17] dipeptides,[18] fructose adducts with amino acids[19] and mixed complexes of amino acids,[16,17] and have found both requirements to be well met. Log K_1 and log β_2 were usually reproduced with an error of < 0.5. As for practicality, with an adequate calibration curve, it took no longer than a few minutes and a PC to calculate the stability constant of any given complex.

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TABLE I. Stability constants (log K_1 and log β_2) of copper(II) mono- and bis-complexes with alanine and alanine derivatives

No.	Ligand	log K_1 (S.E.$_{exp}$) GEP method	log K_1 (S.E.$_{exp}$) SWV method	log β_2 (S.E.$_{exp}$) GEP method	log β_2 (S.E.$_{exp}$) SWV method
1	Alanine	8.15 (1)	8.52 (5)	14.95 (2)	14.76 (6)
2	*N,N*-Dimethylalanine	7.02 (4)	7.66 (2)	13.66 (<1)	13.58 (<1)
3	*N*-Ethylalanine	6.97 (4)	7.12 (6)	12.84 (2)	12.78 (15)
4	*N,N*-Diethylalanine	6.43 (6)	6.79 (4)	12.99 (<1)	12.40 (25)
5	*N*-Propylalanine	7.00 (1)	7.01 (5)	12.82 (4)	13.05 (6)
6	*N,N*-Dipropylalanine	6.47 (8)	6.49 (15)	12.70 (1)	12.76 (22)

The aim of this study was to verify our theoretical method by the classical problem of the validation of stability constants, namely to discuss log K_1 and log β_2 values for copper(II) chelates measured by two electrochemical methods (glass electrode potentiometry, GEP, and square wave voltammetry, SWV). For our study, we chose copper(II) complexes with alanine and its five *N*-alkylated derivatives as determined by these experimental methods in our laboratory.[20] Our constants determined by potentiometry and voltammetry differed from 0.01 to 0.64 and from 0.06 to 0.59 for log K_1 and log β_2, respectively, despite the fact that they were determined under virtually the same experimental conditions (T = 298 K, I(GEP) = 0.1 mol L^{-1} [KNO_3], I(SWV) = 0.15 mol L^{-1} [$NaClO_4$]).

EXPERIMENTAL

Calculation of Topological Indices

The calculations of topological indices were performed with a program system DRAGON 2.1, written by R. Todeschini and coworkers,[21] which is capable of yielding 262 topological indices in a single run along with many other molecular descriptors. Connectivity matrices were constructed with the aid of Online SMILES Translator and Structure File Generator.[22]

As stated previously,[17] the most consistent results were generally obtained using $^3\chi^v$ index (the valence molecular connectivity index of the 3rd order). Thus, in this paper all models were developed using this index, which was defined as:[23–25]

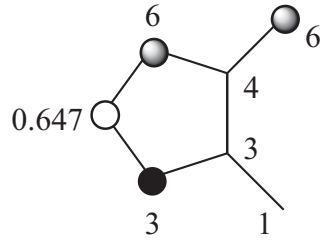
$$^3\chi^v = \sum_{path} [\delta(i)\,\delta(j)\,\delta(k)\,\delta(l)]^{-0.5} \qquad (1)$$

where $\delta(i)$, $\delta(j)$, $\delta(k)$, and $\delta(l)$ are weights (valence values) of vertices (atoms) i, j, k, and l, making up the path of length 3 (three consecutive chemical bonds) in a vertex-weighted molecular graph**.** Valence value, $\delta(i)$, of a vertex i is defined by:

$$\delta(i) = [Z^v(i) - H(i)] \,/\, [Z(i) - Z^v(i) - 1] \qquad (2)$$

where $Z^v(i)$ is the number of valence electrons belonging to the atom corresponding to vertex i, $Z(i)$ is its atomic number, and $H(i)$ is the number of hydrogen atoms attached to it. For instance, delta values for primary, secondary, tertiary, and quaternary carbon atoms are 1, 2, 3, and 4, respectively; for oxygen in OH group 5, and for nitrogen in NH_2 group 3 ($^3\chi^v$ is only a member of a family of valence connectivity indices, $^n\chi^v$, which differ in path length, *i.e.* the number of δ's in the summation term, Eq. (1).

For our calculations we used two kinds of models. The first is derived from constitutional formula (graph) of mono- (ML) and bis-complexes (ML_2). The second is derived from the graphs of diaqua-complexes (ML^{aq} or ML_2^{aq}).[17] Figure 1 shows an example of how connectivity index $^3\chi^v$ is calculated.



$^3\chi^v = (0.647{\cdot}3{\cdot}3{\cdot}4)^{-0.5} + (0.647{\cdot}3{\cdot}3{\cdot}1)^{-0.5} + 2(3{\cdot}3{\cdot}4{\cdot}6)^{-0.5} + 2(1{\cdot}3{\cdot}4{\cdot}6)^{-0.5} + 2\ (3{\cdot}4{\cdot}6{\cdot}0.647)^{-0.5} + (6{\cdot}4{\cdot}6{\cdot}0.647)^{-0.5} + (6{\cdot}0.647{\cdot}3{\cdot}3)^{-0.5} = 1.559$

Figure 1. Scheme for the calculation of connectivity index $^3\chi^v$ for alaninatocopper(II) (see Eq. 1). Valence values are marked at the appropriate vertices (atoms).

Regression Calculations

Regression calculations, including the leave-one-out procedure of cross validation, cv, were done using the CROMRsel program.[26] The standard error of cross validation estimate is defined as:

$$S.E._{cv} = \sqrt{\sum_i \frac{\Delta X_i^{\,2}}{N}} \qquad (3)$$

where ΔX and N denote cv residuals and the number of reference points, respectively.

TABLE II. Stability constants (log K_1 and log β_2) of copper(II) mono- and bis-complexes with aliphatic amino acids and glycine derivatives

No.	Ligand	log K_1	log β_2	Reference
7	Glycine	8.38	15.17	27
8	Alanine	8.15	14.82	28
9	Valine	8.11	14.79	28
10	Leucine	8.11	14.34	29
11	*N*-Methylglycine	7.94	14.59	27
12	*N,N*-Dimethylglycine	7.30	13.65	27
13	*N*-Ethylglycine	7.34	13.55	27
14	*N,N*-Diethylglycine	6.88	12.86	27
15	*N*-Propylglycine	7.25	13.31	27
16	*N*-Butylglycine	7.32	13.52	27
17	*N*-iso-Propylglycine	6.70	12.45	27

RESULTS AND DISCUSSION

Calibration Lines

We estimated the stability constants of two sets of copper(II) complexes. The first set consisted of six copper(II) complexes with alanine and its *N*-alklylated derivatives (Table I). The second set (Table II) included copper(II) chelates with glycine, its seven *N*-alkylated derivatives, and three aliphatic amino acids (alanine, valine, and leucine).

For the first set, the calibration lines were derived from stability constants measured in our laboratory using GEP and SWV (Tables III and IV).[20] The second set of the calibration lines[17] (Table V) was derived from constants measured with GEP, compiled from the literature.[27-29] All models better reproduced log K_1 values than log β_2, *i.e.* S.E.$_{cv}$ was 0.30–0.54 and 0.57–1.06 for log K_1 and log β_2, respectively. This is in accordance with our previous findings, namely that log K_1 was generally reproduced with smaller error than log β_2.[17,19]

The differences between two experimental methods (GEP and SWV) are reflected in regression parameters presented in Tables III and IV. Connectivity indices better correlate to log K_1(GEP), r = 0.947–0.957, than to log K_1(SWV), r = 0.851–0.902. For log β_2 the opposite trend was observed, r = 0.711–0.765 and 0.792–0.862 for GEP and SWV, respectively. Log β_2 for *N*-alkylated glycinates (Table V), based on the S.E.$_{cv}$ values (because r's are not directly comparable), was better reproduced than the constants for alaninates, irrespective of the experimental method used. However, log K_1 values for glycinates were better reproduced only in respect to the SWV constants for alaninates.

TABLE III. Linear regressions of log K_1(GEP) and log β_2(GEP) on the connectivity index $^3\chi^v$; ligands **1**–**6**, Table I

Regression No.	Dependent variable	Independent variable	Intercept (S.E.)	Slope (S.E.)	r	S.E.	S.E.$_{cv}$
1	log K_1	$^3\chi^v$(ML)	8.95 (34)	–0.69 (12)	0.947	0.18	0.35
2	log K_1	$^3\chi^v$(ML^{aq})	9.17 (34)	–0.540 (82)	0.957	0.16	0.30
3	log β_2	$^3\chi^v$(ML$_2$)	15.8 (11)	–0.32 (14)	0.751	0.52	0.95
4	log β_2	$^3\chi^v$(ML$_2^{aq}$)	15.7 (12)	–0.23 (12)	0.711	0.56	1.06
5	log β_2	$^3\chi^v$(ML)	15.51 (95)	–0.78 (33)	0.765	0.51	0.88
6	log β_2	$^3\chi^v$(ML^{aq})	15.7 (11)	–0.58 (26)	0.740	0.53	0.97

TABLE IV. Linear regressions of log K_1(SWV) and log β_2(SWV) on the connectivity index $^3\chi^v$; ligands **1**–**6**, Table I

Regression No.	Dependent variable	Independent variable	Intercept (S.E.)	Slope (S.E.)	r	S.E.	S.E.$_{cv}$
7	log K_1	$^3\chi^v$(ML)	9.43 (54)	–0.77 (18)	0.902	0.29	0.46
8	log K_1	$^3\chi^v$(ML^{aq})	9.51 (72)	–0.56 (17)	0.851	0.35	0.54
9	log β_2	$^3\chi^v$(ML$_2$)	15.90 (89)	–0.35 (11)	0.840	0.42	0.71
10	log β_2	$^3\chi^v$(ML$_2^{aq}$)	15.8 (10)	–0.256 (99)	0.792	0.47	0.82
11	log β_2	$^3\chi^v$(ML)	15.64 (74)	–0.86 (25)	0.862	0.39	0.66
12	log β_2	$^3\chi^v$(ML^{aq})	15.78 (89)	–0.64 (22)	0.828	0.44	0.73

TABLE V. Linear regressions of log K_1 and log β_2 on the connectivity index $^3\chi^v$; ligands **7**–**17**, Table II

Regression No.	Dependent variable	Independent variable	Intercept (S.E.)	Slope (S.E.)	r	S.E.	S.E.$_{cv}$
13	log K_1	$^3\chi^v$(ML)	9.03 (49)	–0.74 (25)	0.708	0.38	0.44
14	log K_1	$^3\chi^v$(ML^{aq})	9.64 (42)	–0.68 (14)	0.858	0.28	0.37
15	log β_2	$^3\chi^v$(ML$_2$)	17.23 (72)	–0.57 (12)	0.845	0.45	0.61
16	log β_2	$^3\chi^v$(ML$_2^{aq}$)	17.06 (75)	–0.395 (92)	0.819	0.48	0.57
17	log β_2	$^3\chi^v$(ML)	16.27 (72)	–1.21 (36)	0.749	0.56	0.66
18	log β_2	$^3\chi^v$(ML^{aq})	17.05 (68)	–1.04 (22)	0.845	0.45	0.59

TABLE VI. Estimation of log K_1 for copper(II) complexes with aliphatic amino acids and glycine derivatives from regression models given in Table III and IV

	Experimental log K_1	Estimates with model			
		1	2	7	8
Glycine	8.38	8.21	8.18	8.61	8.49
Alanine	8.15	7.87	7.96	8.22	8.26
Valine	8.11	7.56	7.72	7.88	8.01
Leucine	8.11	7.50	7.67	7.81	7.96
N-Methylglycine	7.94	7.99	7.71	8.36	7.99
N,N-Dimethylglycine	7.30	7.80	7.32	8.15	7.59
N-Ethylglycine	7.34	7.60	7.50	7.92	7.78
N,N-Diethylglycine	6.88	6.79	6.71	7.03	6.96
N-Propylglycine	7.25	7.56	7.48	7.89	7.75
N-Butylglycine	7.32	7.37	7.32	7.67	7.60
N-iso-Propylglycine	6.70	7.33	7.34	7.63	7.61
mean	7.59	7.60	7.54	7.92	7.82
rms		0.38	0.30	0.51	0.37

Estimation of Stability Constants of Copper(II) Aminoacidates

To verify our method and discuss experimental results we estimated log K_1 and log β_2 values of glycinates from regression models developed on alaninates (Tables VI and VII) and *vice versa* (Table VIII). The rms error of log K_1 for glycinates (Table VI) was in the range of 0.30–0.51 which is comparable to the S.E.$_{cv}$ range of 0.37–0.44 obtained by direct regression (Table V). The same holds true for log β_2 (rms = 0.53–0.61 *vs.* S.E.$_{cv}$ = 0.57–0.66).

Data presented in Tables VI and VII make it also possible to compare GEP and SWV. Log K_1 is better reproduced by models developed from the constants obtained by GEP (Models 1 and 2, Table III). Not only did they show better rms values (0.30–0.38 *vs.* 0.37–0.51), but they also yielded smaller systematic error, as show the mean values (7.60 and 7.54 *vs.* 7.92 and 7.82; experimental = 7.59). For log β_2 values (Table VII) the opposite yet less pronounced trend was observed (0.55–0.61 *vs.* 0.53–0.59). This again is in accordance with the previous finding (*c.f.* paragraph *Calibration Lines*) that theoretical results better fit log K_1 values obtained by GEP and log β_2 values obtained by SWV.

Table VIII shows the final comparison of GEP and SWV, where log K_1 and log β_2 for alaninates were estimated from the calibration lines developed on glycinates. Rms(log K_1) values were substantially better for GEP (0.19–0.23) than for SWV (0.42–0.51), and rms(log β_2) spanned the range of 0.72–0.85 and 0.59–0.70 for GEP and SWV, respectively. This is another indication that GEP yields better log K_1 values than SWV, and that the opposite is true for log β_2 values.

Comparison of Theoretical and Experimental Values

The validity of our estimation was verified by linear regression of GEP to SWV constants. Log β_2(GEP) is

TABLE VII. Estimation of log β_2 for copper(II) complexes with aliphatic amino acids and glycine derivatives from regression models given in Table III and IV

	Exp.	Estimates with model							
	log β_2	3	4	5	6	9	10	11	12
Glycine	15.17	14.63	14.49	14.69	14.59	14.65	14.49	14.72	14.61
Alanine	14.82	14.37	14.34	14.30	14.36	14.36	14.33	14.29	14.35
Valine	14.79	14.08	14.13	13.95	14.1	14.05	14.10	13.91	14.07
Leucine	14.34	14.03	14.09	13.88	14.05	13.99	14.06	13.83	14.01
N-Methylglycine	14.59	14.14	13.87	14.43	14.08	14.11	13.82	14.44	14.05
N,N-Dimethylglycine	13.65	13.77	13.39	14.22	13.67	13.71	13.29	14.21	13.60
N-Ethylglycine	13.55	13.88	13.77	13.99	13.86	13.83	13.71	13.96	13.81
N,N-Diethylglycine	12.86	13.02	12.99	13.09	13.01	12.89	12.86	12.96	12.87
N-Propylglycine	13.31	13.85	13.75	13.96	13.83	13.80	13.68	13.92	13.78
N-Butylglycine	13.52	13.68	13.62	13.74	13.67	13.61	13.54	13.67	13.60
N-iso-Propylglycine	12.45	13.69	13.66	13.70	13.69	13.62	13.59	13.63	13.62
rms		0.55	0.56	0.61	0.55	0.53	0.56	0.59	0.53

TABLE VIII. Estimation of log K_1 and log β_2 for copper(II) complexes with alanine and its derivatives from regression models given in Table V

	Estimates with model					
	13	14	15	16	17	18
Alanine	7.87	8.12	14.71	14.78	14.38	14.73
N,N-Dimethylalanine	7.15	6.76	12.70	12.58	13.19	12.64
N-Ethylalanine	7.15	7.19	13.25	13.46	13.19	13.30
N,N-Diethylalanine	6.23	6.14	11.60	12.08	11.69	11.69
N-Propylalanine	7.10	7.15	13.18	13.42	13.11	13.24
N,N-Dipropylalanine	6.25	6.15	11.63	12.09	11.71	11.71
rms (for GEP)	0.19	0.23	0.85	0.72	0.76	0.83
rms (for SWV)	0.42	0.51	0.70	0.60	0.59	0.68

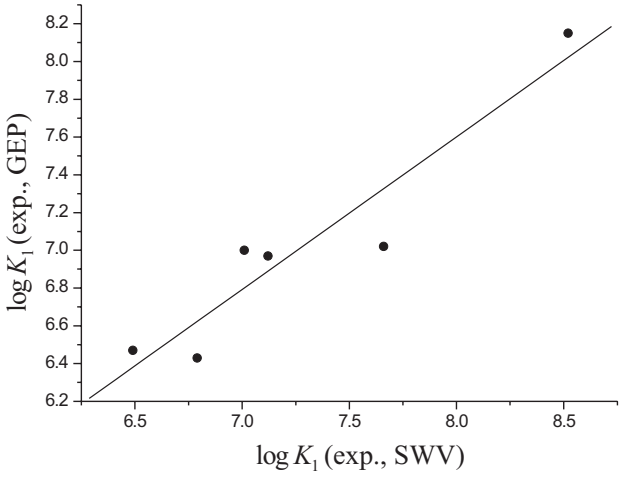


Figure 2. Regression line for the correlation of log K_1(GEP) to log K_1 (SWV). Slope = 0.81(14), intercept = 1.1(10), r = 0.946.

highly correlated to log β_2(SWV), r = 0.948, as well as log K_1(GEP) to log K_1(SWV), r = 0.946 (Figure 2). Interesting to note, the correlation of log K_1 values obtained by the two experimental methods is of the same quality as the correlation of log K_1(GEP) to its values estimated from Model 14 (Table VIII), yielding r = 0.957.

The plot of experimental errors, expressed as S.E.$_{exp}$,[20] *vs.* difference between estimated and measured log K_1(GEP) shows a statistically significant correlation (Figure 3), as well as log β_2(SWV) does, but less pronounced (p = 0.38). Conversely, Δlog K_1(SWV) and Δlog β_2 (GEP) do not correlate with their appropriate experimental errors (S.E.). These results suggest that log K_1(GEP) and log β_2(SWV) values are essentially free from systematic error. The difference between log K_1(GEP) and log K_1(SWV) values is the highest for the complexes with alanine, *N,N*-dimethylalanine, and

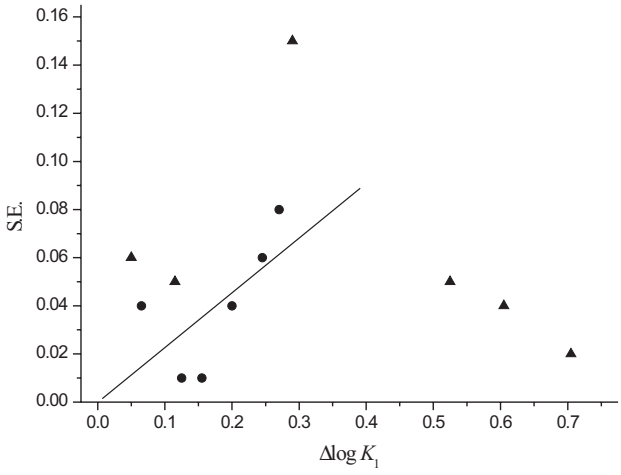


Figure 3. Regression line of the standard experimental error ($S.E._{exp}$) to the absolute difference between experimental (GEP) and mean of two (Models 13 and 14, Table VIII) estimated log K_1 values. Slope = 0.247(130), intercept = – 0.004(2), r = 0.689, p = 0.13. Data for SWV method (not included in regression) were marked with ▲.

N,N-diethylalanine (0.37, 0.64, and 0.36, respectively), as well as the difference between theoretical and SWV values (0.5–0.7, Figure 3). All these indicate some kind of systematic error in log K_1(SWV).

CONCLUSION

The comparison between experimental and theoretical results leads to three conclusions: 1) the theoretical method reproduces experimental constants in the error range commensurable to the differences between GEP and SWV, 2) GEP gives more reliable values for log K_1 constants than SWV, and 3) SWV gives more reliable values for log β_2 than GEP.

The second conclusion is supported by the fact that data for log K_1(GEP) constants were determined in the pH range where the response of glass electrode is due only to the formation of ML species. Data for log K_1(SWV) constants were measured around the detection limit for determination of peak potential shift ($\Delta E_p \leq 2$ mV). Overall stability constants, that is, log β_2(SWV), are more reliable because voltammetry allows measurements at a low total metal ion concentration and large total ligand to total metal ion concentration ratios, which postpones or minimizes the extent of hydrolysis.[30–32]

However, ideally, GEP and SWV yield the same values of stability constants for the same complexes. In our case these ideal conditions were not met, and log K_1 values for complexes with alanine, *N,N*-dimethylalanine, and *N,N*-diethylalanine determined with SWV showed a disagreement with the GEP constants. As the SWV constants for those three complexes were also worst reproduced by our theoretical models, we judge the values of log K_1(SWV) constants for alanine, *N,N*-dimethylalanine, and *N,N*-diethylalanine as problematic.

There is no such theory in chemistry that could replace the experiment. However, a theory could help experimentalists in planning experiments and discussing their results. We hope that our simple theoretical method for estimation of stability constants achieves this end.

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SAŽETAK

Ocjena dviju elektroanalitičkih metoda za određivanje konstanti stabilnosti upotrebom graf-teorijskih modela

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Konstante stabilnosti K_1 i β_2 bakrovih(II) kompleksa s alaninom i pet njegovih *N*-alkiliranih i *N*,*N*-dialkiliranih derivata mjerene potenciometrijski staklenom elektrodom (GEP) i kvadratnom valnom voltametrijom (SWV), procijenjivane su upotrebom graf-teorijskih modela. Korelacije s indeksom povezanosti trećega reda, $^3\chi^v$, pokazuju da su vrijednosti log K_1(GEP) bolje procijenjene (S.E. = 0,18–0,16) od vrijednosti log K_1(SWV), S.E. = 0,29–0,35. Obratno je za vrijednosti log β_2 (S.E. = 0,51–0,56 (GEP), 0,39–0,47 (SWV)). Primjena triju kriterija – (1) razlika vrijednosti GEP i SWV, (2) razlika SWV i teorijskih vrijednosti te (3) korelacija eksperimentalnih pogrešaka ($S.E._{exp}$) prema razlici eksperimentalnih i teorijskih vrijednosti – ukazuje da su tri eksperimentalne vrijednosti log K_1(SWV) upitne. Stoga ovaj rad pokazuje da su nedavno razvijeni graf-teorijski modeli korisni u planiranju eksperimenta i raspravi o njima dobivenim rezultatima.