3rd European NECTAR Conference
Ljubljana, August 24th-26th 2022

Comparative study on the current tools for optimization of stability constants from potentiometric data

WG4

DEVELOPMENT OF TOOLS, SERVICES AND FACILITIES FOR THE NECTAR COMMUNITY

Silvia BERTO,[a] Salvador BLASCO,[b] Lorenzo CASTELLINO,[a] Aleksandar CVETKOVSKI,[c] Sofia GAMA,[d] Enrique GARCÍA-ESPAÑA,[b] Petr HERMANN,[e] Vojtěch KUBÍČEK,[e] Gabriele LANDO,[f] Michel MEYER,[g] Demetrio MILEA,[f] Winfried PLASS,[h] Lauryn QUINODOZ, [g]

a) Università di Torino, Dipartimento di Chimica, via P. Giuria 7, 10125 Torino, Italy
b) Institute of Molecular Sciences, University of Valencia, c/Catedrático José Beltrán Martínez 2, 46980 Paterna, Valencia, Spain
c) Faculty of Medical Sciences, Goce Delcev Universit, Krste Misirkov bb, 2000 Štip, PO 201, N. Macedonia
d) University of Bialystok, Faculty of Chemistry, Department of Analytical Chemistry, K. Ciolkowskiego 1K, 15-245 Bialystok, Poland
e) Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 40 Prague 2, Czech Republic
f) Università degli Studi di Messina, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, CHIBIOFARAM, V.le F. Stagno d'Alcontres, 31, 98166 Messina, Italy
g) Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR 6302, CNRS, Université Bourgogne–Franche-Comté, 9 avenue Alain Savary, BP 47870, 21078 Dijon, France
h) Institut für Anorganische &und Analytische Chemie, Friedrich Schiller University Jena, Humboldtstr 8, D-07743 Jena, Germany

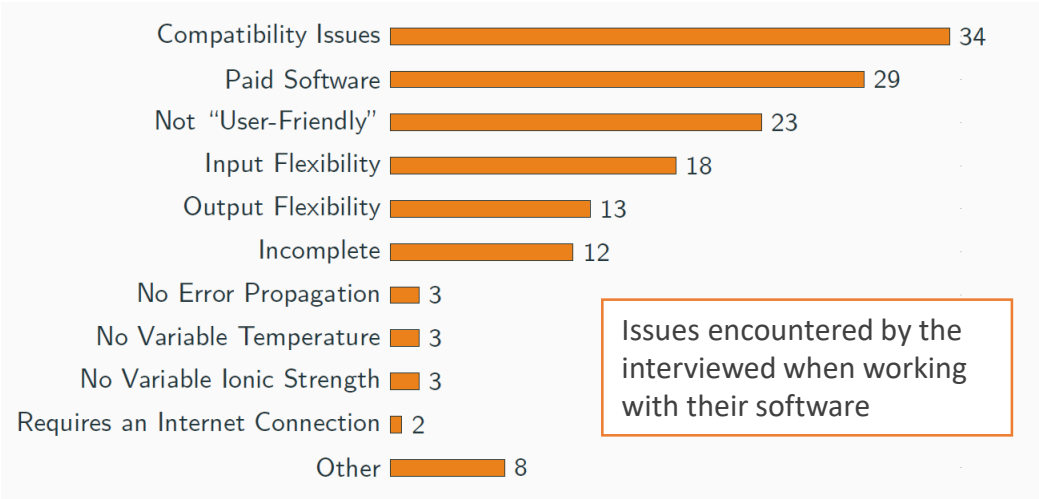
3rd European NECTAR Conference
Ljubljana, August 24th-26th 2022

WG4 DEVELOPMENT OF TOOLS, SERVICES AND FACILITIES FOR THE NECTAR COMMUNITY

TASK: PROVIDING UPDATED GUIDELINES, SOFTWARE AND SERVICES TO ENHANCE THE PERFORMANCES OF BOTH RESEARCH AND APPLICATIONS IN EQUILIBRIUM THERMODYNAMICS

1

Survey conducted on 64 of the participants of COST ACTION 18202, "Network for Equilibria and Chemical Thermodynamics Advanced Research" (NECTAR) in 2020



Issues encountered by the interviewed when working with their software

The survey highlights the **need of the development of new IT tools** for the management of chemical equilibria in solution by the NECTAR community

Development of a multi-platform and open-source software, dedicated to the analysis of potentiometric data

2 **Development of PyES** - an open source software for the computation of in solution and precipitation equilibria

3 **Critical evaluation of the software actually available** for the analysis of potentiometric data, in order to identify the strengths and weaknesses of each and to use this knowledge for the development of new IT products

3

Tested software :

Hyperquad[1,2]
BSTAC[3]
SUPERQUAD[4]
OPIUM[5]
K-ev[6]
Reactlab suite[7]

Dataset:

six different titrations conducted on a **hypothetic hexaprotic acid**

Formation constants to be refined

species	logβ	log$K$
AH^{5-}	10	10
AH_2^{4-}	18	8
AH_3^{3-}	24	6
AH_4^{2-}	28	4
AH_5^{-}	31	3
AH_6	33	2

Titration conditions

titrant	KOH 0.1000	mol/L
initial volume	25.0	mL
temperature	25.0	°C
ionic strength	0.10	mol/L

Components concentrations

A^{6-}	2.0	4.0	5.0	mmol/L
H^+	12.0	24.0	30.0	mmol/L

Calibration data

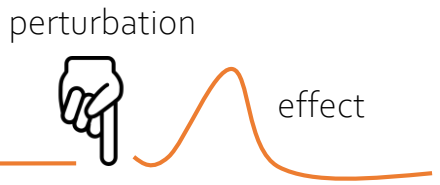
E^0	405.0	mV
Nernstian slope	-59.16	mV
j_A	-64	mV L/mol
pK_w	-13.77	

[1] P. Gans, A. Sabatini, A. Vacca, Talanta 1996, 43, 1739-1753.
[2] http://www.hyperquad.co.uk/HQ2013.htm
[3] C. De Stefano, P. Mineo, C. Rigano, S. Sammartano, Annali di Chimica (Rome) 1993, 83, 243-277.
[4] P. Gans, A. Sabatini, A. Vacca, Inorganica Chimica Acta 1983, 79, 219-220.
[5] https://web.natur.cuni.cz/~kyvala/opium.html
[6] https://k-ev.org/
[7] https://jplusconsulting.com/

The data analysis was carried out including some **systematic errors** in the calculation, quite common in the experimental procedures

3

- ✓ Evaluate the impact of systematic errors arising in potentiometry on the refined parameters
- ✓ Check the sensitivity of the different software in relation to these errors



Systematic errors

titrant carbonation	0.0980 mol/L (instead 0.1000 mol/L)
incorrect calibration	E^0 = 406 mV (instead 405 mV)
calibration without junction potential	j_A neglected and theoretical pK_w = 13.78
purity of the acid	impurity 2% of the nominal concentration
ionic strength changes	constants refinement with fixed or variable ionic strength

3 ✓ Not all software have the same features

Tested software	handle more than one titration	treat j_A value	optimize the components concentrations	work with variable ionic strength
Hyperquad	☑	⊗	☑	⊗
BSTAC	☑	☑	☑	☑
SUPERQUAD	☑	⊗	☑	⊗
OPIUM	☑	☑	✓*	⊗
K-ev	⊗	⊗	⊗	⊗
Reactlab suite	☑	☑	☑	⊗

* OPIUM does not allow simultaneous refinement of concentration in experiments with different concentration values.

NETWORK FOR EQUILIBRIA AND CHEMICAL THERMODYNAMICS ADVANCED RESEARCH

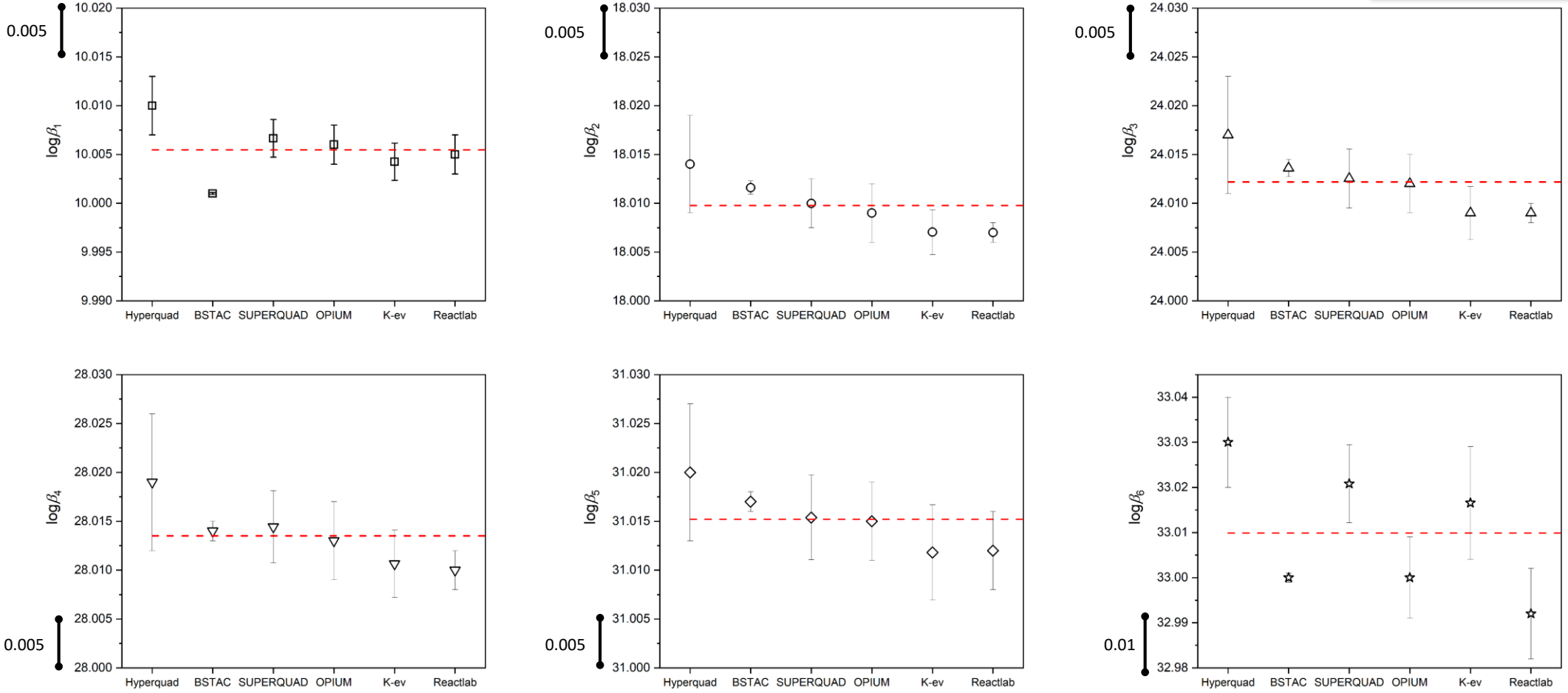
EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

K-ev cannot process more than one titration. Thus, the results reported are the mean values, and the corresponding standard deviations, obtained processing the titration one-by-one

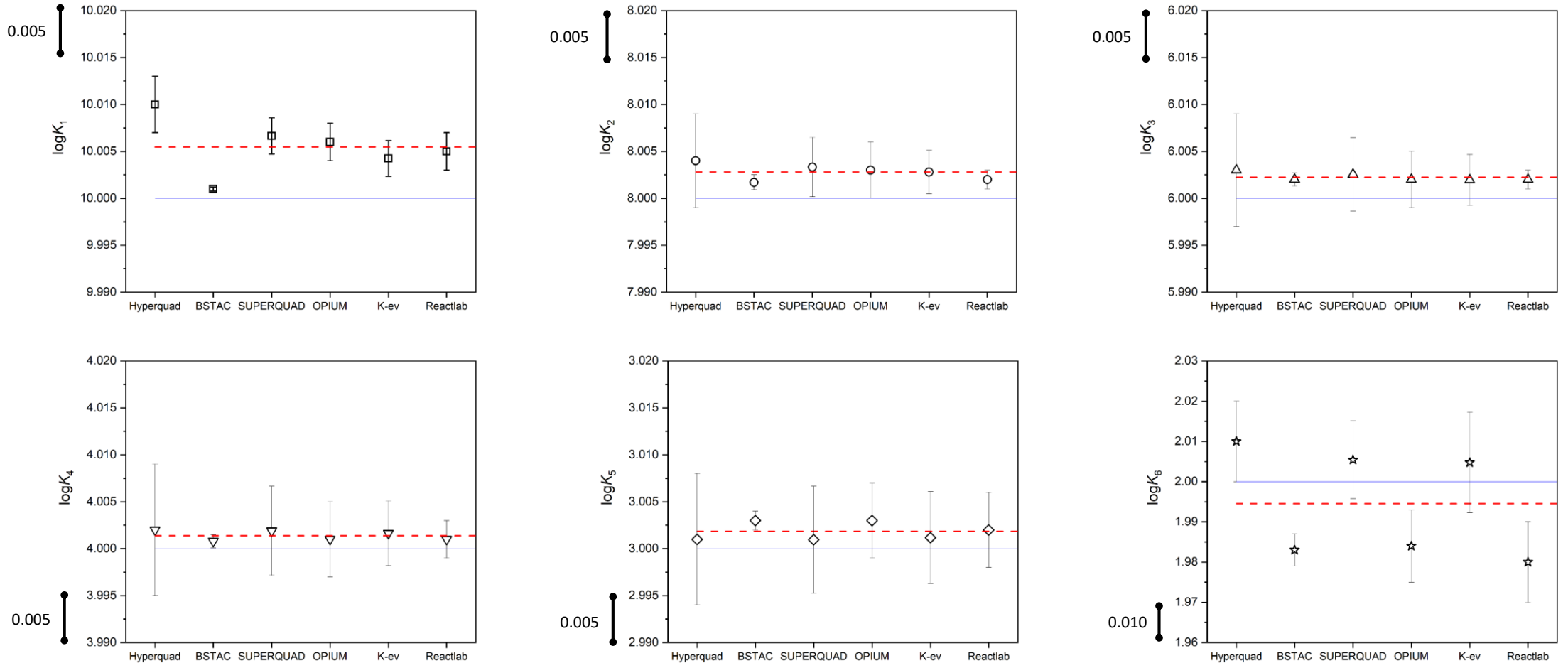
Others $w = \frac{1}{s^2}$

BSTAC $w = \frac{1}{s^n}$ $n = 0.5, 0.75, 1$

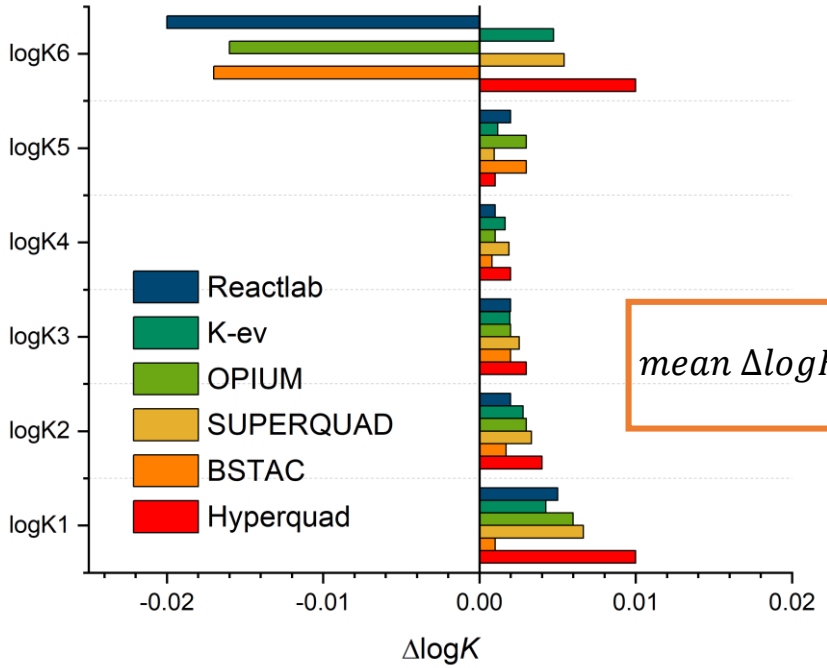
Estimated logβ



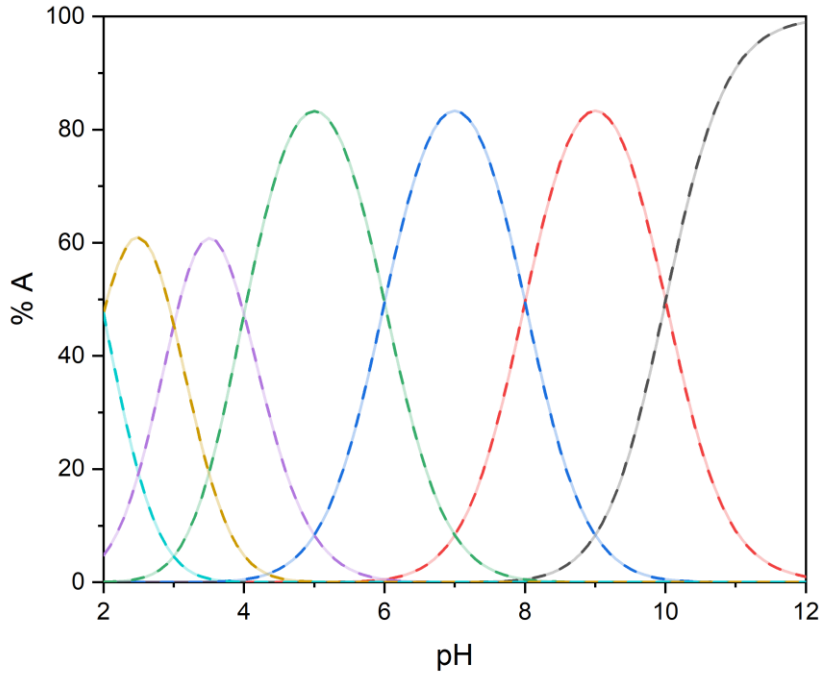
Estimated log*K*



Refined vs theoretical



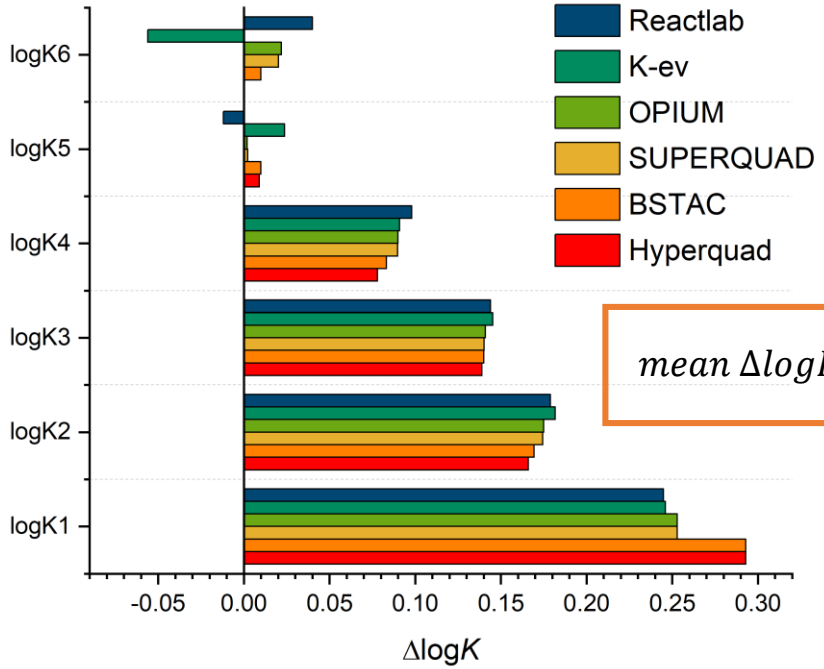
$$mean\ \Delta logK \approx 0.001 \Rightarrow \frac{K'}{K} \approx 1.002$$



Solid line: theoretical protonation constants
Dotted line: refined mean protonation constants

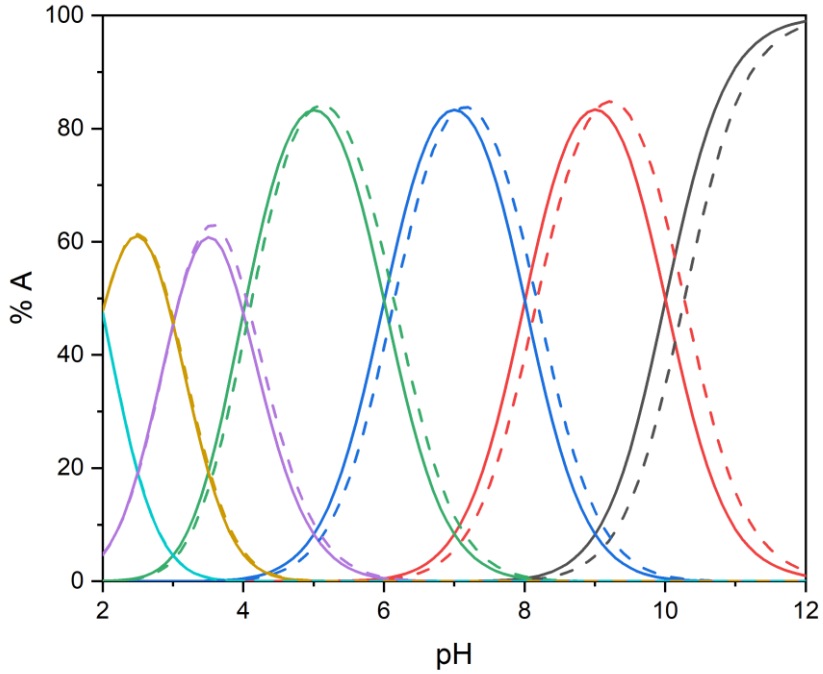
Titrant carbonation

KOH 0.098 mol/L instead 0.100 mol/L



$$mean\ \Delta logK \approx 0.113$$

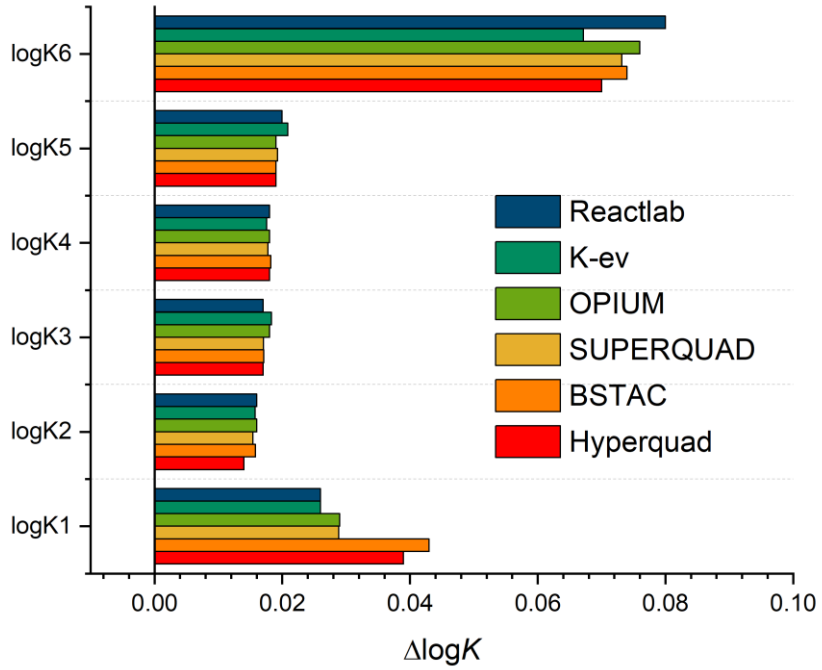
$$\frac{K'}{K} \approx 1.3$$



Solid line: refined mean protonation constants with KOH 0.100 mol/L
Dotted line: refined mean protonation constants with KOH 0.098 mol/L

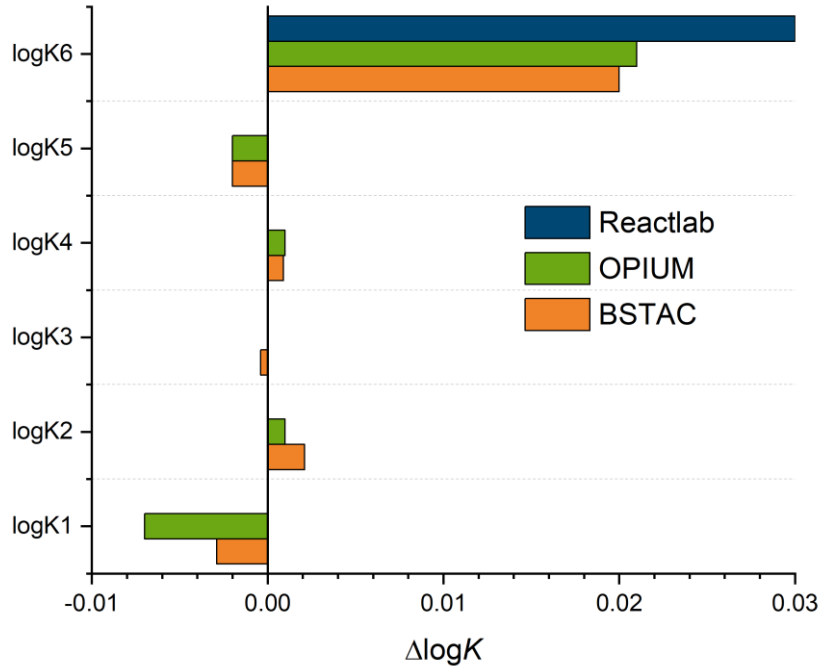
Error in calibration outcome

E^o 406.0 mV instead 405.0 mV



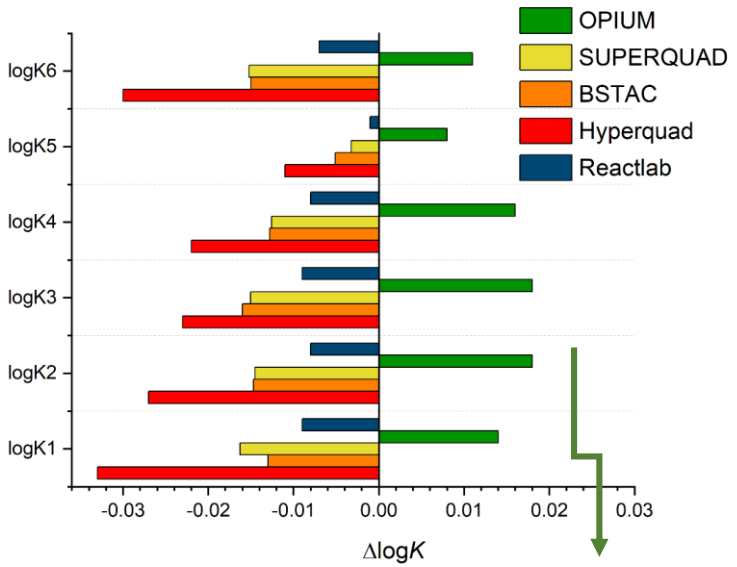
$$mean\ \Delta logK \approx 0.03 \Rightarrow \frac{K'}{K} \approx 1.07$$

Junction potential neglected



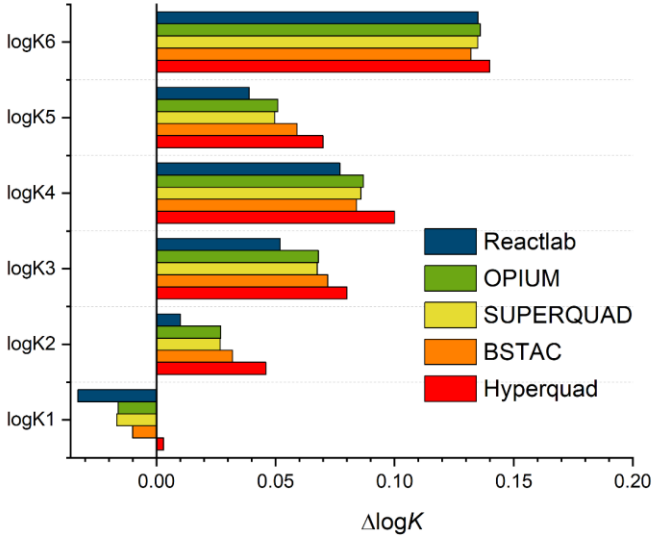
Bias with respect the reference conditions: fixed concentrations of both A^{6-} and H^+

fixed nominal concentrations of A^{6-}
refined concentration of H^+



OPIUM does not allow simultaneous refinement of concentration in experiments with different concentration values. Thus, the concentration was refined for each couple of titrations separately and the obtained values were used for refinement of protonation constants.

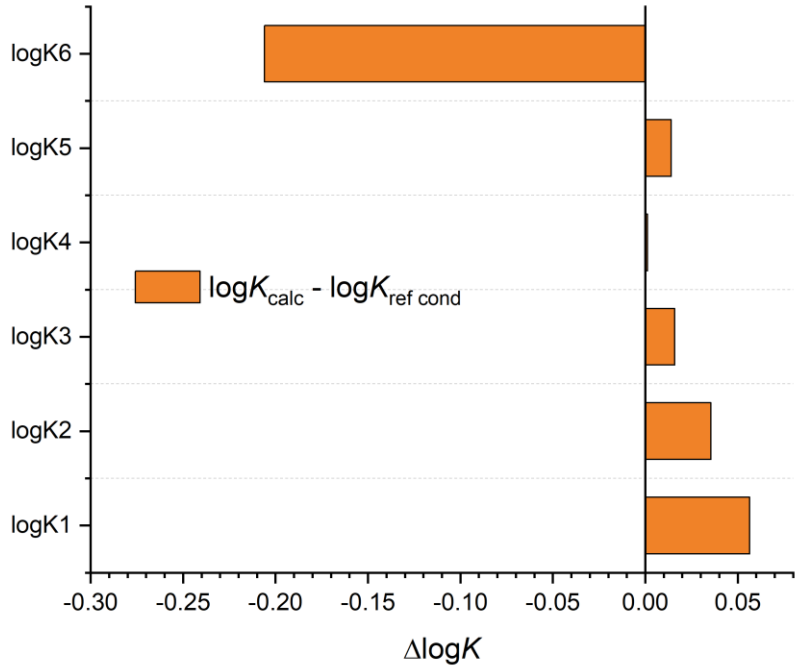
A^{6-} with impurity of 2%
Refined concentration of H^+

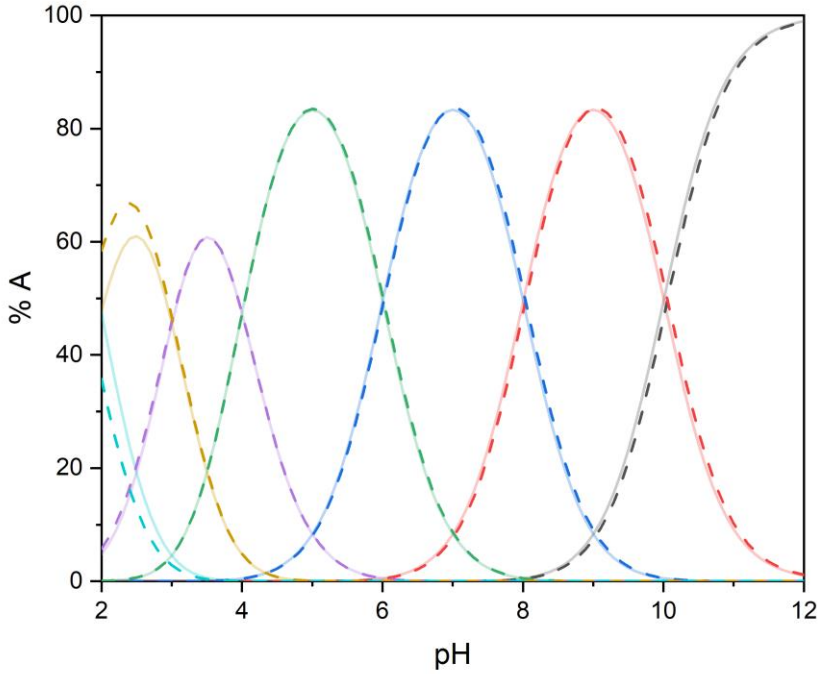


$$mean\ \Delta logK \approx 0.06 \Rightarrow \frac{K'}{K} \approx 1.15$$

Variable ionic strength (BSTAC)

I = 0.130 - 0.116 mol/L





Solid line: refined mean protonation constants with fixed ionic strength
Dotted line: refined mean protonation constants with variable ionic strength

Concluding remarks

3 **Critical evaluation of the software actually available**

Key points:

Develop new IT products with all desired functionalities

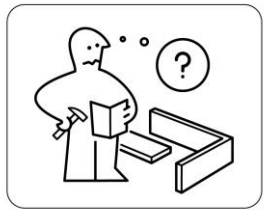
How manage uncertainty

Evaluate the impact of systematic errors arising in potentiometry on the refined parameters

4

Useful to define guidelines for good laboratory practice

Useful to define guidelines for data analysis



WG4

DEVELOPMENT OF TOOLS, SERVICES AND FACILITIES FOR THE NECTAR COMMUNITY

TASK: PROVIDING UPDATED GUIDELINES, SOFTWARE AND SERVICES TO ENHANCE THE PERFORMANCES OF BOTH RESEARCH AND APPLICATIONS IN EQUILIBRIUM THERMODYNAMICS

NECTAR
NETWORK FOR EQUILIBRIA AND CHEMICAL THERMODYNAMICS ADVANCED RESEARCH

cost
EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY

3rd European NECTAR Conference
Ljubljana, August 24th-26th 2022

Thank you for your attention