

MINFIT: A Spreadsheet-based Tool for Parameter Estimation in an Equilibrium Speciation Software Program

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Supporting Information

Please visit MINFIT Website: <http://minfit.strikingly.com> to download the updated tutorials and the .mif files for the examples.

Content	Page
Part I	
Extended discussion about mass action equation.....	S1
Extended discussion about data extraction and processing.....	S2-S3
Extended discussion about the weighting factor.....	S4
Extended discussion about fitting parameter limitations.....	S5
Figure S1. Screenshot of MINFIT interface.....	S6
Table S1. Summary of illustrative examples.....	S7
Table S2-S4. Details about the examples.....	S7-S9
Table S5. Raw data for the examples.....	S10-S11
References.....	S11-S12
Part II	
Step-by-step tutorial of MINFIT with three examples.....	T1-T28

Mass Action Equation for Multidentate Surface Reactions

It should be noted that the standard state of surface species used in MINEQL+, including the most recent version, remains to be 1.0 mole/L, in contrast to the more robust fraction-based or site-occupancy-based standard states.¹⁻³ Although representing surface species' activity by molar concentration is acceptable for monodentate species, the equilibrium constants for multidentate surface reactions become dependent on the amount of sorbent (i.e., total site concentrations). As long as the total site concentration is not a variable in the "Field Data" input, which means the experimental results were all obtained at a fixed solid concentration and the site density was not a fitting parameter, then parameter estimation problems involving multidentate surface complexation can still be handled by MINFIT. The users need to acknowledge that the molarity referenced equilibrium constants are applicable to the specific total site concentration.¹⁻⁵ In some cases when both multidentate surface reaction and variation of total site concentration are involved, then the MINFIT generated "Field Data" must be corrected. More details of such conversion can be found in Wang and Giammar.⁶ The future necessity of updating MINFIT to address this issue will depend on whether the next version of MINEQL+ changes this fundamental setting to be consistent with recent versions of other programs (e.g., Visual MINTEQ, PHREEQC, ECOSAT), that is to use mole or coverage fraction of the total site concentration as the activity metrics of surface species.

Additional Details about Data Extraction and Processing

MINEQL+ loads the “Field Data” text file and runs the problem under the “Field Data” option, where the meanings of each column of the text file are defined. The “Field Data” calculation results are opened by the MINEQL+ “Output Manager”, which allows the results to be extracted in versatile formats. MINFIT is programmed to require MINEQL+ to display the results for each species in the “obs \times variable” format (more information in MINEQL+ manual) and save them as a two-column txt file. The first column is recommended to be set as the name of the species, and the second column is selected according to the specific problem (e.g., concentration, logC, %, activity, etc.). The results are saved to the MINFIT-created blank text files in the order that is consistent with the datasets.

Subsequently, MINFIT reads the files and displays those results in the “MINEQL Output” tab, which are called in the subsequent calculations performed in the “Calibration” tab. MINFIT allows users to freely define the objective function by manually editing the formula in the “Calibration” tab, if needed, in forms not readily reportable by MINEQL+ (e.g., the ratio of two concentrations). An illustrative example is provided in the tutorial of the Supporting Information.

In the “Calibration” tab, MINFIT computes the residual sum of squares (RSS) from calculations for each parameter set and displays the optimal solution in this round of search in the “Summary” tab. A transparent interface allows the user to examine every calculation.

MINFIT includes a “Review Residual” button that allows users to selectively examine a certain range of simulation results by entering a threshold residual. MINFIT sorts those simulations with residuals from low to high and generates hyperlinks to each. The hyperlinks are coded with a command to paste all the corresponding results to the “Summary” tab, allowing the users to individually examine and plot the specific results. The searches can be repeated until the parameter sets are narrowed down to a smaller range where a minimum RSS value may be located (Figure 1).

Additional Discussion about the Weighting Factor

The option to allow users to enter the weighting factor table is useful when accurate estimates for error in the data are available, or when there is uncharacteristically high uncertainty associated with just a few data points (i.e., high uncertainty corresponds to small weighting factor). A WSOS/DF value close to unity indicates that the difference between model and the experiment is close to the experimental errors.⁷ Pragmatically, values smaller than 0.1 indicate a poorly constrained system (i.e., too large of experimental errors), and values larger than 20 indicate poor fit (i.e., too large of differences between model and experiment).⁸ The default settings of MINFIT impose $W = 1$ unless the users edit them. If no experimental error is assigned, then the goodness of fit can be simply interpreted as RSS or SOS/DF, and the lowest value indicates the best fit.

Additional Discussions about Fitting Parameter Limitation of MINFIT

MINEQL+ allows the “Field Data” to contain various types of inputs, i.e., Fixed Ion (e.g., pH), log K , Gases, ΔH , Total Concentration, and Special (e.g., temperature, solid concentration, specific surface area, ionic strength), in which ionic strength was newly included in version 5.0. Those options are sufficient for most chemical equilibrium problems. However, MINEQL+ still does not allow capacitances, which are required in the constant capacitance model (CCM) and triple layer model (TLM), to be entered in the “Field Data”. Therefore, capacitance cannot be treated as a fitting parameter unless MINEQL+ is specifically updated. There are some cases in which pH_{zpc} is a constraint (i.e., ΔpK_a of the surface protonation reactions is a fitting parameter), but MINEQL+ does not allow such input directly. Nevertheless, it is convenient to use the spreadsheet calculator to modify MINFIT-generated “Field Data” to be equivalent to fixing pH_{zpc} with varying ΔpK_a .

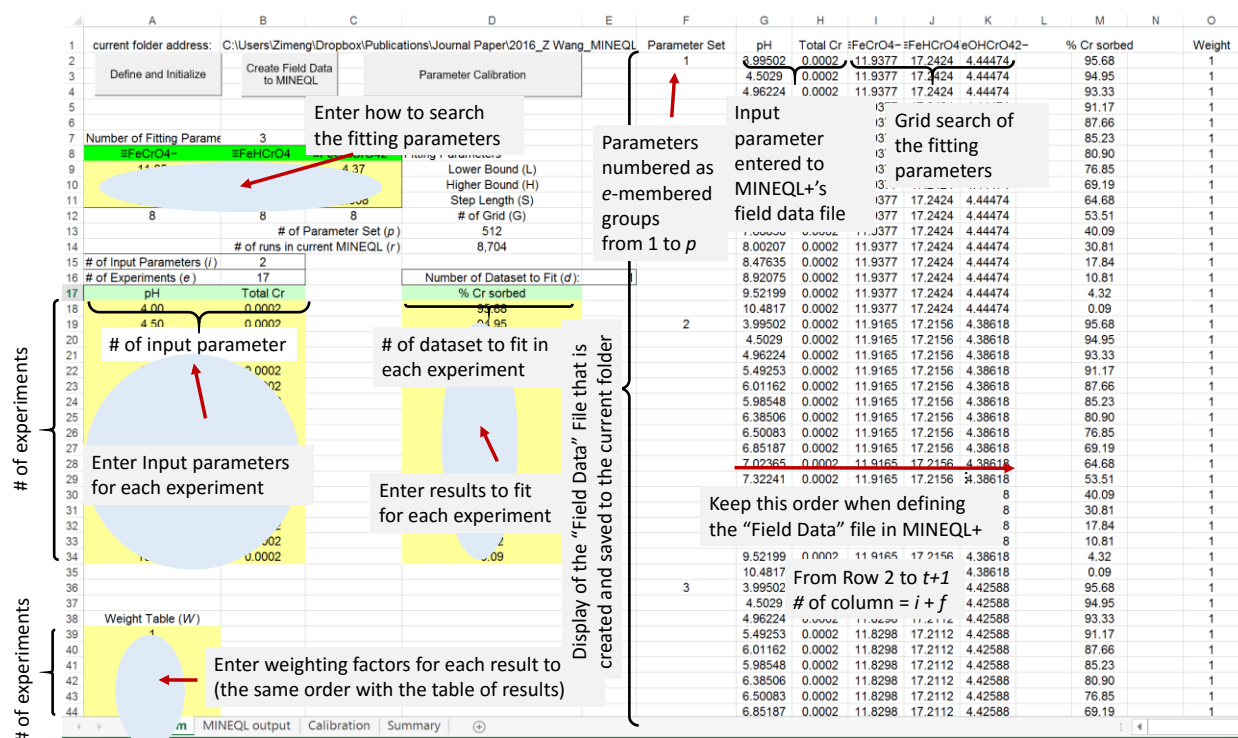


Figure S1. Screenshot of the Problem Tab of MINFIT with explanatory information about how the interface works. Note that the screenshot only shows the first 44 rows of the spreadsheet, which actually has 8,705 rows. After generating and displaying the “Field Data”, the total row of the spreadsheet should be $r + 1$.

Table S1. Summary of the three illustrative examples in this study.

Parameter in MINFIT	Cu complexation with pyromellitic acid	Chromate adsorption to goethite	Sulfate adsorption to ferrihydrite
Model type	Aqueous Speciation	Double Layer	Triple Layer
Objective	LogC	% Adsorbed	% Surface Species
Number of searches taken	3	5	3
Number of fitting parameters (<i>f</i>)	2	3	2
Number of input parameters (<i>i</i>)	2	1	1
Number of datasets to fit (<i>d</i>)	1	1	2
Number of experiments (<i>e</i>)	42	17	5

Table S2. The aqueous speciation model of Example 1: Cu complexation with pyromellitic acid

Equilibrium Reactions ^a	Log $K_{I=0}$ ^b	Log $K_{I=0.1\text{ M}}$ ^b	Log K^0 ^c	Log $K_{I=0.1\text{ M}}$ ^c
Cu pyromellitic complexation (to be determined)				
$\text{Cu}^{2+} + \text{L}^{4-} + \text{H}^+ \rightleftharpoons \text{CuHL}^-$	11.0	9.72	10.2	8.77
$\text{Cu}^{2+} + \text{L}^{4-} \rightleftharpoons \text{CuL}^{2-}$	5.40	3.69	5.60	3.90
Pyromellitic acid protonation and Cu hydrolysis (fixed) ^d				
$\text{L}^{4-} + \text{H}^+ \rightleftharpoons \text{HL}^{3-}$	6.20	5.35	6.20	5.35
$\text{L}^{4-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{L}^{2-}$	11.10	9.61	11.10	9.61
$\text{L}^{4-} + 3\text{H}^+ \rightleftharpoons \text{H}_3\text{L}^-$	14.22	12.29	14.22	12.29
$\text{L}^{4-} + 4\text{H}^+ \rightleftharpoons \text{H}_4\text{L}_{(\text{aq})}$	15.91	13.77	15.91	13.77
$\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-7.71	-8.14	-7.71	-8.14
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_{2(\text{aq})} + \text{H}^+$	-16.21	-16.86	-16.21	-16.86
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} + 2\text{H}^+$	-10.31	-10.96	-10.31	-10.96
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	-13.997	-13.783	-13.997	-13.783

^a The conversion of conditional equilibrium at different ionic strength was based on the Davies equation.

^b The Cu pyromellitic complexation constants obtained by MINFIT in the present example. MINEQL+ calculates problems using equilibrium constants at zero ionic strength.

^c The Cu pyromellitic complexation constants obtained by Giammar and Dzombak⁹ by using FITEQL. For a comparison of the quality of fitting between that of the previous study and of MINFIT in the present study, see Figure 2 of Giammar and Dzombak and Figure 2 in the present paper.

^d The constants for 0.1 M ionic strengths were from Giammar and Dzombak⁹ (see original references therein). Those constants are first converted to zero ionic strength condition and then used in MINEQL+ calculation, which automatically determines activity coefficients using the Davies equation.

Table S3. The aqueous speciation model of Example 2: Chromate adsorption to goethite^a

Equilibrium Reactions ^b	Log K^0 ^c	Log K^0 ^d
<i>Chromate surface complexation reaction (to be determined)</i>		
$\equiv\text{FeOH} + \text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \equiv\text{FeCrO}_4^- + \text{H}_2\text{O}$	11.87	11.92
$\equiv\text{FeOH} + \text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \equiv\text{FeHCrO}_4 + \text{H}_2\text{O}$	17.19	17.09
$\equiv\text{FeOH} + \text{CrO}_4^{2-} \rightleftharpoons \equiv\text{FeOHCrO}_4^{2-}$	4.42	4.334
<i>Other reactions (fixed)</i>		
$\equiv\text{FeOH} + \text{H}^+ \rightleftharpoons \equiv\text{FeOH}_2^+$		6.93
$\equiv\text{FeOH} \rightleftharpoons \equiv\text{FeO}^- + \text{H}^+$		-9.65
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$		-13.997
$2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$		14.56
$\text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HCrO}_4^-$		6.51
$\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{CrO}_{4(\text{aq})}$		6.419

^a Mathur and Dzombak fixed the site density, specific surface area and surface acid-base reactions of goethite, and used FITEQL to fit adsorption data from independent peer-reviewed publications and reported intrinsic equilibrium constants for zero ionic strength in a unified framework. They acknowledged that when there are more than two fitting parameters, FITEQL frequently failed to converge, so that iterative forward calculations were performed for the best fit.¹⁰ For simplicity, they employed the monodentate surface complexation reactions and acknowledged that those reactions were selected simply for simulating macroscopic adsorption equilibrium rather than reflecting the actual molecular-scale surface speciation.¹¹ The same premise was adopted in the compilation of the database for hydrous ferric oxide¹² and gibbsite¹³.

^b Generalized double layer model for goethite as developed by Mathur and Dzombak¹⁰ with a unified specific surface area of 60 m²/g, and site density of 2 sites/nm². The surface protonation/deprotonation reactions as well as the chromate aqueous speciation reactions were also fixed as in Mathur and Dzombak's model. Equilibrium constants are all corresponding to zero ionic strength.

^c Equilibrium constants obtained using MINFIT (Figure 3) by fitting the data of Mesuere and Fish¹⁴ at 0.2 M total chromate and 1.8 g/L goethite at 0.1 M ionic strength.

^d Equilibrium constants obtained by Mathur¹⁵ using FITEQL. The SOS/DF (no weighting factor or experimental error was considered) was 0.7. The SOS/DF calculated by MINFIT is 0.88. The tiny difference is probably caused by the error during our digitalization of the graphic data in Mesuere and Fish's original publication.

Table S4. The aqueous speciation model of Example 3: Sulfate adsorption to ferrihydrite

Equilibrium Reactions ^a	ψ_0	ψ_β	LogK ^b
<i>Sulfate inner- and outer-sphere surface complexation (to be determined)</i>			
$2\equiv\text{FeOH} + 2\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons (\equiv\text{FeO})_2\text{SO}_2 + 2\text{H}_2\text{O}$	0	0	15.5 ^c
$\equiv\text{FeOH} + 2\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \equiv\text{FeOH}_2^+ \text{--} \text{HSO}_4^-$	+1	-1	19.2
<i>Ferrihydrite (de)protonation and electrolyte adsorption (fixed)</i>			
$\equiv\text{FeOH} + \text{H}^+ \rightleftharpoons \equiv\text{FeOH}_2^+$	+1	0	3.7
$\equiv\text{FeOH} \rightleftharpoons \equiv\text{FeO}^- + \text{H}^+$	-1	0	-12.1
$\equiv\text{FeOH} + \text{Na}^+ \rightleftharpoons \equiv\text{FeO}^- \text{--} \text{Na}^+ + \text{H}^+$	-1	+1	-19.9
$\equiv\text{FeOH} + \text{H}^+ + \text{NO}_3^- \rightleftharpoons \equiv\text{FeOH}_2^+ \text{--} \text{NO}_3^-$	+1	-1	11.9
<i>Aqueous Reactions (fixed)</i>			
$\text{SO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_4^-$	N.A.	N.A.	1.98
$\text{SO}_4^{2-} + \text{Na}^+ \rightleftharpoons \text{NaSO}_4^-$	N.A.	N.A.	0.88
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	N.A.	N.A.	-13.997

^a Extended triple layer model for ferrihydrite as developed by Fukushima and Sverjensky¹⁶ with a unified specific surface area of 600 m²/g, and site density of 3.8 sites/nm². Capacitance $C_1 = 100 \mu\text{F}/\text{cm}^2$, $C_2 = 20 \mu\text{F}/\text{cm}^2$. For the present model simulation, the total sulfate concentration is 1 mM, ionic strength is 0.02 M as NaNO₃ and ferrihydrite concentration is 2.45 g/L.

^b Equilibrium constants are all corresponding to zero ionic strength. Only the sulfate surface complexation reactions were optimized by fitting the XANES derived surface speciation data. The surface protonation/deprotonation and outer sphere electrolyte complexation reactions were selected based on Fukushima and Sverjensky¹⁶. More details can be found in Gu et al.¹⁷

^c For the bidentate surface reaction, the reported LogK here is only applicable for 2.45 g/L ferrihydrite condition. For more information about the how to convert it for other solid loadings, see Wang and Giammar⁶. Unlike previous sulfate surface complexation models, Gu et al. used a bidentate binuclear inner surface complex, which was supported by extended X-ray absorption fine structure data.

Table S5. Raw data used in the three illustrative examples (displayed as entered in MINFIT as input parameters and experimental results, other fixed, non-field-data parameters are specified in the text and figure captions).

Table S5a. Cu complexation with pyromellitic acid

pH	Total Cu(M)	Log [Cu] _{Total} ^a	Measured Log[Cu ²⁺]	pH	Total Cu (M)	Log [Cu] _{Total}	Measured Log[Cu ²⁺]
3	2.04E-06	-5.69	-6.02	4	8.32E-07	-6.08	-6.97
3	8.32E-06	-5.08	-5.46	4	2.09E-06	-5.68	-6.61
3	2.04E-05	-4.69	-5.05	4	8.32E-06	-5.08	-6
3	8.13E-05	-4.09	-4.43	4	2.04E-05	-4.69	-5.57
3	2.00E-04	-3.7	-4	4	8.13E-05	-4.09	-4.95
3	7.94E-04	-3.1	-3.36	4	2.00E-04	-3.7	-4.49
3	1.95E-03	-2.71	-2.92	4	7.94E-04	-3.1	-3.82
5	8.51E-07	-6.07	-7.63	4	2.00E-03	-2.7	-3.37
5	2.09E-06	-5.68	-7.26	5.75	2.04E-07	-6.69	-8.16
5	8.51E-06	-5.07	-6.72	5.75	6.46E-07	-6.19	-7.78
5	2.09E-05	-4.68	-6.28	5.75	1.26E-06	-5.9	-7.46
5	8.32E-05	-4.08	-5.67	5.75	7.59E-06	-5.12	-6.87
5	2.04E-04	-3.69	-5.21	5.75	2.00E-05	-4.7	-6.47
5	8.13E-04	-3.09	-4.57	5.75	8.13E-05	-4.09	-5.84
5	2.00E-03	-2.7	-4.13	5.75	2.00E-04	-3.7	-5.45
6.75	1.91E-07	-6.72	-7.94	5.75	7.94E-04	-3.1	-4.86
6.75	7.94E-07	-6.1	-7.53	5.75	2.00E-03	-2.7	-4.44
6.75	2.00E-06	-5.7	-7.18	5.75	3.16E-03	-2.5	-4.37
6.75	7.94E-06	-5.1	-6.61				
6.75	2.00E-05	-4.7	-6.21				
6.75	7.94E-05	-4.1	-5.64				
6.75	1.95E-04	-3.71	-5.26				
6.75	7.76E-04	-3.11	-4.73				
6.75	1.91E-03	-2.72	-4.48				

^a The logarithms of total Cu concentration were reported in tables in Giammar and Dzombak⁹ and were easier for graphing. However, as input parameter of MINFIT and MINEQL+, they were converted to actual molar concentrations.

Table S5b. Chromate adsorption to goethite

pH	Measured Adsorbed Cr (%)
4.00	95.68
4.50	94.95
4.96	93.33
5.49	91.17
6.01	87.66
5.99	85.23
6.39	80.90
6.50	76.85
6.85	69.19
7.02	64.68
7.32	53.51
7.69	40.09
8.00	30.81
8.48	17.84
8.92	10.81
9.52	4.32
10.48	0.09

The data were digitalized from the publication of Mesuere and Fish¹⁴ in print. The fitting results using the unified goethite surface complexation database¹⁵ were provided by David Dzombak and are available in the thesis of Mathur.¹⁵

Table S5c. Sulfate adsorption to ferrihydrite

pH	Measured $\equiv\text{FeOH}_2^+ \text{--} \text{HSO}_4^-$ (%)	Measured $(\equiv\text{FeO})_2\text{SO}_4$ (%)
3	57.3	42.6
5	72.4	26.18
6	70.9	12.58
7	35.1	7.69
8	14.2	2.68

The fractions were based on the total sulfate loading and calculated by the macroscopic adsorption percentage and the relative contributions of outer and inner sphere complexations quantified using linear combination fittings of XANES spectra. Details can be found in Gu et al.¹⁷

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Step-by-step Tutorials for MINFIT

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Example 1. Cu complexation with pyromellitic acid

Problem Description: Giammar and Dzombak determined the formation constants of copper complexes with the mellitic acids using potentiometric titrations at five pH values.¹ FITEQL was used to optimize the equilibrium constants to fit the data. Testing various possible complexes revealed that the simple 1:1 complexes of CuL and CuHL (L denotes the fully deprotonated acid) could describe all the data. We select the data set of Cu complexation with pyromellitic acid ($C_6H_2(C_2O_3)_2$) to illustrate MINFIT's capability to reproduce their fitting. The following tables summarize the experimental data and the aqueous speciation model they built.

Raw data for the problem of Cu complexation with 10 mM total pyromellitic acid.

pH	Total Cu(M)	Log [Cu] _{Total} ^a	Measured Log[Cu ²⁺]	pH	Total Cu (M)	Log [Cu] _{Total}	Measured Log[Cu ²⁺]
3	2.04E-06	-5.69	-6.02	4	8.32E-07	-6.08	-6.97
3	8.32E-06	-5.08	-5.46	4	2.09E-06	-5.68	-6.61
3	2.04E-05	-4.69	-5.05	4	8.32E-06	-5.08	-6
3	8.13E-05	-4.09	-4.43	4	2.04E-05	-4.69	-5.57
3	2.00E-04	-3.7	-4	4	8.13E-05	-4.09	-4.95
3	7.94E-04	-3.1	-3.36	4	2.00E-04	-3.7	-4.49
3	1.95E-03	-2.71	-2.92	4	7.94E-04	-3.1	-3.82
5	8.51E-07	-6.07	-7.63	4	2.00E-03	-2.7	-3.37
5	2.09E-06	-5.68	-7.26	5.75	2.04E-07	-6.69	-8.16
5	8.51E-06	-5.07	-6.72	5.75	6.46E-07	-6.19	-7.78
5	2.09E-05	-4.68	-6.28	5.75	1.26E-06	-5.9	-7.46
5	8.32E-05	-4.08	-5.67	5.75	7.59E-06	-5.12	-6.87
5	2.04E-04	-3.69	-5.21	5.75	2.00E-05	-4.7	-6.47
5	8.13E-04	-3.09	-4.57	5.75	8.13E-05	-4.09	-5.84
5	2.00E-03	-2.7	-4.13	5.75	2.00E-04	-3.7	-5.45
6.75	1.91E-07	-6.72	-7.94	5.75	7.94E-04	-3.1	-4.86
6.75	7.94E-07	-6.1	-7.53	5.75	2.00E-03	-2.7	-4.44
6.75	2.00E-06	-5.7	-7.18	5.75	3.16E-03	-2.5	-4.37
6.75	7.94E-06	-5.1	-6.61				
6.75	2.00E-05	-4.7	-6.21				
6.75	7.94E-05	-4.1	-5.64				
6.75	1.95E-04	-3.71	-5.26				
6.75	7.76E-04	-3.11	-4.73				
6.75	1.91E-03	-2.72	-4.48				

^aThe logarithms of total Cu concentration was reported in tables in Giammar and Dzombak¹ and were easier for graphing. However, as input parameter of MINFIT and MINEQL+, they were converted to actual molar concentrations.

The aqueous speciation model of Example 1: Cu complexation with 10 mM total pyromellitic acid

Equilibrium Reactions ^a	Log $K_{I=0}$ ^b	Log $K_{I=0.1\text{ M}}$ ^b	Log K^0 ^c	Log $K_{I=0.1\text{ M}}$ ^c
Cu pyromellitic complexation (to be determined)				
$\text{Cu}^{2+} + \text{L}^{4-} + \text{H}^+ \rightleftharpoons \text{CuHL}^-$	11.0	9.72	10.2	8.77
$\text{Cu}^{2+} + \text{L}^{4-} \rightleftharpoons \text{CuL}^{2-}$	5.40	3.69	5.60	3.90
Pyromellitic acid protonation and Cu hydrolysis (fixed) ^d				
$\text{L}^{4-} + \text{H}^+ \rightleftharpoons \text{HL}^{3-}$	6.20	5.35	6.20	5.35
$\text{L}^{4-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{L}^{2-}$	11.10	9.61	11.10	9.61
$\text{L}^{4-} + 3\text{H}^+ \rightleftharpoons \text{H}_3\text{L}^-$	14.22	12.29	14.22	12.29
$\text{L}^{4-} + 4\text{H}^+ \rightleftharpoons \text{H}_4\text{L}_{(\text{aq})}$	15.91	13.77	15.91	13.77
$\text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuOH}^+ + \text{H}^+$	-7.71	-8.14	-7.71	-8.14
$\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_{2(\text{aq})} + \text{H}^+$	-16.21	-16.86	-16.21	-16.86
$2\text{Cu}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{OH})_2^{2+} + 2\text{H}^+$	-10.31	-10.96	-10.31	-10.96
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	-13.997	-13.783	-13.997	-13.783

^a The conversion of conditional equilibrium at different ionic strength was based on the Davies equation.

^b The Cu pyromellitic complexation constants obtained by MINFIT in the present example. MINEQL+ calculates problems using equilibrium constants at zero ionic strength.

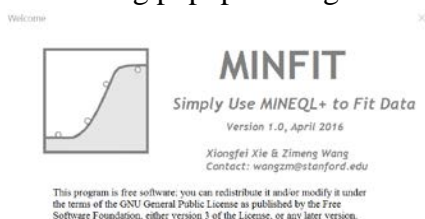
^c The Cu pyromellitic complexation constants obtained by Giammar and Dzombak¹ by using FITEQL. For a comparison of the quality of fitting between that of the previous study and of MINFIT in the present study, see Figure 2 of Giammar and Dzombak and Figure 2 in the present paper.

^d The constants for 0.1 M ionic strengths were from Giammar and Dzombak¹ (see original references therein). In MINFIT, those constants were converted to zero ionic strength condition and used in MINEQL+ calculation, which automatically determines activity coefficients using the Davies equation.

After the users have a sense of how MINFIT works, the problem demonstrated in this tutorial can be accomplished in less than 20 min.

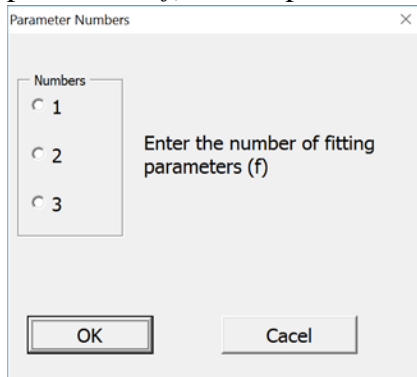
Part 1. Initialize and define the problem in MINFIT

- (1) It is recommended to first rename or “save as” the downloaded MINFIT program after the specific project title to avoid overwriting. Open MINFIT and see the welcoming popup message. Enable Macros in Excel.

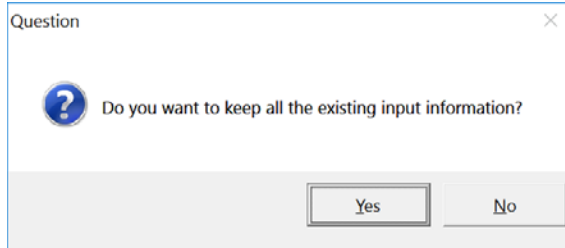


- (2) In the “Problem” tab, click “Define and Initialize”. See a popup message box “The following operation will delete all but one dataset to fit in Tab ‘Calibration’”, and

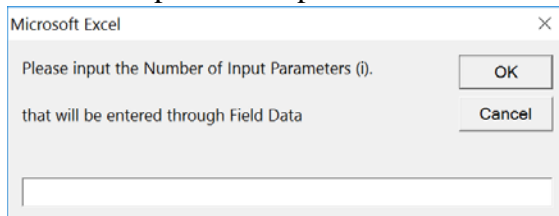
click OK. Another popup window asks the users to select the number of fitting parameters (f) for the problem.



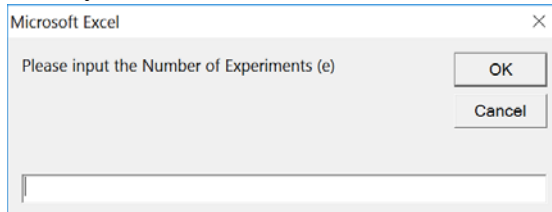
- (3) Here we select “2” for the example. Then a popup window asks “Do you want to keep all the existing input information?” When initializing the problem for the first time, select “No” so that you can then add the necessary information. When doing iterative search with all the needed information already entered, select “Yes” and proceed to “Create Field Data to MINEQL” step.



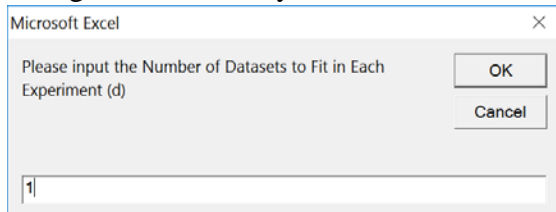
- (4) We selected “No” in the last step. Then a popup box asks you to enter the Number of Input Parameters (i). Recall from Table 1 that there are two input parameters that varies in experiments: pH and total Cu. Then enter “2”.



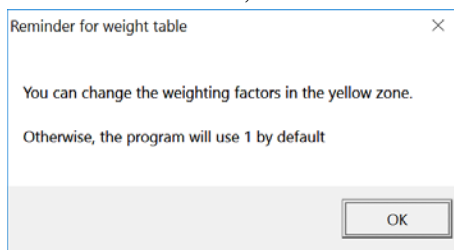
- (5) Then a popup window asks you to enter the Number of Experiments (e). This is exactly the total number of entries in Table 1. Enter “42”.



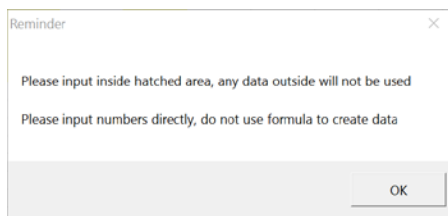
- (6) Then a pop-up box asks you to enter the Number of Datasets to Fit in Each Experiment (d). In the problem, only the measured $\log[\text{Cu}^{2+}]$ is considered in the fitting. Therefore only 1 dataset is fitted in each experiment. Enter “1”.



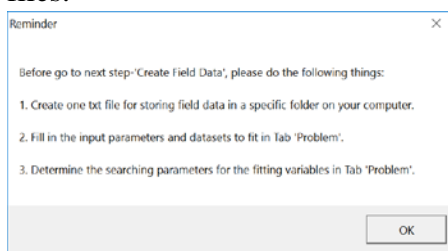
- (7) After finishing all the entries above, MINFIT refreshes the spreadsheet and delineates the yellow-hatched cells for the users to enter data. Then a popup box reminds the users about the weighting factor table, which is displayed on the lower left corner of tab “Problem” tab. The dimensions of the weighting factor table are identical to those of the experimental results (e rows \times d columns). Since the example does not involve different weighting factors, click OK and leave the weighting factor table as 1 by default. Otherwise, the table can be manually edited.



- (8) A popup box reminds the users to only input values inside the hatched area and to not use formula to create data so as to avoid program failure.



- (9) A pop-up box tells the users to fill in all the input parameters and experimental data to fit in a certain format in the “Problem” tab. Also it is time to identify a folder to store all the MINFIT generated field and create an empty txt file for storing the field data. In just a few steps the users will need to browse the folder to select and write to the files.



- (10) The users can paste the information as in Table 1 to the yellow-hatched cells in the “Problem” tab. The green-hatched cells can be edited freely to designate the names of the values below. The unit of those values should be consistent with the default units

used in MINEQL+ (e.g., concentration and ionic strength is mole/L, sorbent concentration is g/L, specific surface area is m²/g). For the unit of the dataset to fit, it is at users' discretion to decide which one to use, as MINEQL+ can export %, Log C, and molar concentrations. For this example, logC will be entered for the experimental data. Below is a partial screenshot to illustrate how data were entered in MINFIT.

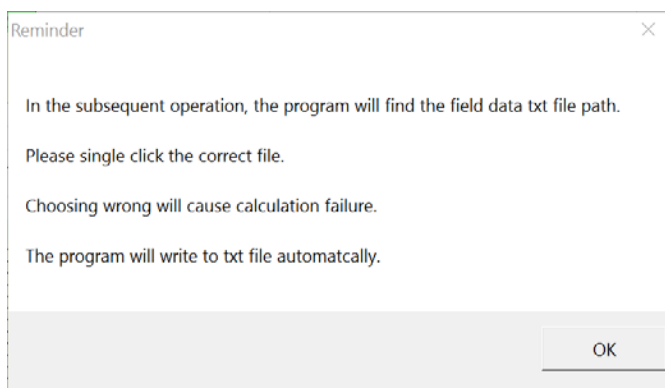
	A	B	C	D	E
1	current folder address:	C:\Users\Zimeng\Dropbox\Publications\Journal Paper\2016_Z Wang_Pa			
2	Define and Initialize	Create Field Data to MINEQL	Parameter Calibration		
3					
4					
5					
6					
7	Number of Fitting Parameters (f)	2			
8	CuL(2-)	CuHL(-)		Fitting Parameters	
9				Lower Bound (L)	
10				Higher Bound (H)	
11				Step Length (S)	
12	1	1	1	# of Grid (G)	
13		# of Parameter Set (p)		1	
14		# of runs in current MINEQL (r)		42	
15	# of Input Parameters (i)	2			
16	# of Experiments (e)	42		Number of Dataset to Fit (d):	1
17	pH	Total Cu		Log [Cu2+]_measured	
18	3	2.04174E-06		-6.02E+00	
19	3	8.31764E-06		-5.46E+00	
20	3	2.04174E-05		-5.05E+00	
21	3	8.12831E-05		-4.43E+00	
22	3	0.000199526		-4.00E+00	

- (11) The next step is to define the search ranges of the two fitting parameters. Enter the name of each fitting parameter in the green cells as above. To start, search -5 to 20 for the two log Ks with fairly rough grids. The step length (S) is tuned to be 2 for each dimension so that the total runs in MINEQL (r) would take acceptable amount of computation time (a couple of minutes). This is to avoid a bug in MINEQL+4.6, but MINEQL+ 5.0 does not have this limitation. It is at the users' choice to make the tradeoff between the computation time for each search and the number of different search.

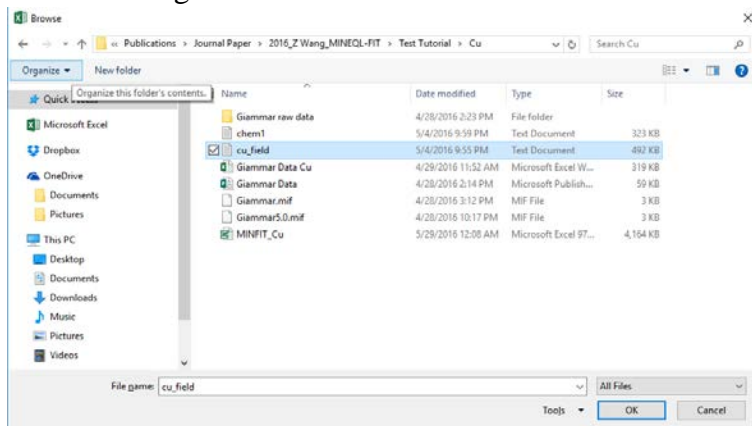
7	Number of Fitting Parameters (f)	2		
8	CuL(2-)	CuHL(-)		Fitting Parameters
9	-5	-5		Lower Bound (L)
10	20	20		Higher Bound (H)
11	2	2		Step Length (S)
12	13	13	1	# of Grid (G)
13		# of Parameter Set (p)		169
14		# of runs in current MINEQL (r)		7,098

Part 2. Create “Field Data” to MINEQL+

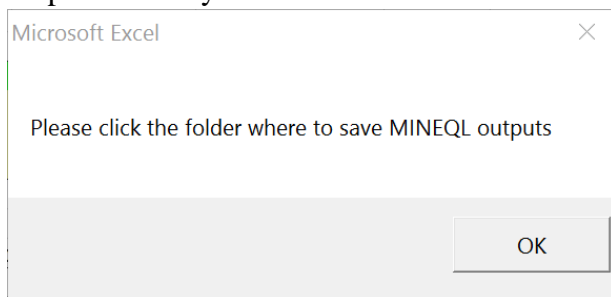
- (1) After all the information of the input parameters, experimental data, and the fitting parameters is entered in the “Problem” tab, click “Create Field Data to MINEQL”. A popup box explains the operation.



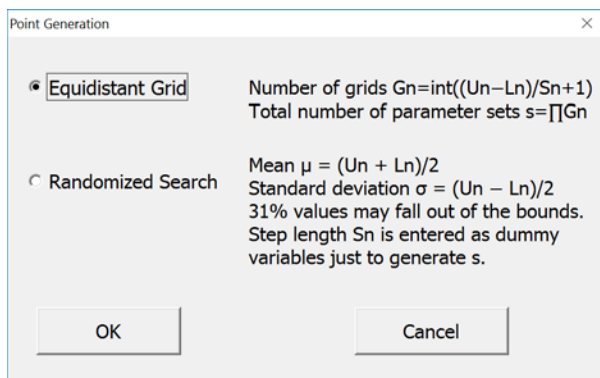
Either at this point or earlier, the users need to create an empty txt file on their hard drive. It is recommended to create the txt file in a dedicated folder to save all the related files for the specific project and name the file with recognizable file name. The file will store the MINFIT generated “Field Data”. Usually in the subsequent iterative search steps, one can just overwrite the previous txt file. Then click “OK” to see a “Browse” window. Here the users can select the specific txt file, “cu_field”, which is designated to store the “Field Data” for this example, and click OK.



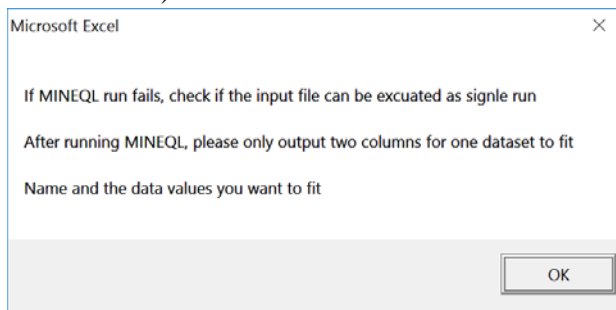
- (2) Another popup box reminds the users to select the folder where to save the MINEQL outputs. Usually it can be the same folder where the “Field Data” txt file is located.



- (3) Then the users are asked to how to generate the “Field Data” file. For more information, refer to the manuscript that describes MINFIT. For initial screening, select Exhaustive Grid search method.

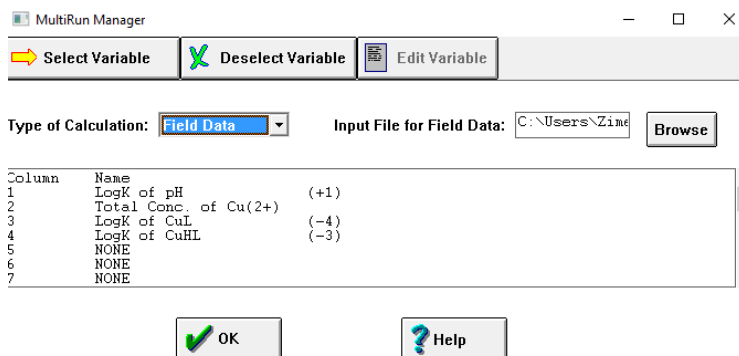


- (4) Then MINFIT computes for the “Field Data” table, displays the values on the right hand side of the “Problem” tab, and saves it as a space-delimited txt file to the previously designated path and file. Note that the first row of the “Field Data” displayed in MINFIT simply indicates the meaning of each column, and that they are not saved to the txt file. The users will need to define the meaning of each column of values later in MINEQL+. A popup message tells about how to export the results from MINEQL+ and allow MINFIT to read them automatically (more details in the next section).



Part 3. Run the “Field Data” file on MINEQL+

- (1) The aqueous speciation model is set up in MINEQL+ (4.6 in this tutorial, the process identical for other versions. One can refer to the manual and tutorials. The .mif file is also provided at the MINFIT website). To invoke the “Field Data” processing, the users need to go to MultiRun and select Field Data, browse and select the path for the “Field Data” txt file to be read by MINEQL+.
- (2) The users need to define the “Field Data” file so that MINEQL+ understands what each column means. Use Select Variable to select those variables in the same order as shown in those screenshots above. The input parameters come first followed by the fitting parameters. MINEQL+ limits the total number of columns in the “Field Data” below 25, so $d+f < 25$.



- (3) Run MINEQL+. It may take a few minutes depending on the problem's complexity and the computing power of the processor.
- (4) Use the built-in Output Manager of MINEQL+ to export the results that are corresponding to those in the "Problem" tab as data to fit. MINFIT was programmed to automatically recognize txt files with results tabulated into two columns. The first column is the name of the output and the second column is the values. Basic knowledge of the Output Manager of MINEQL+ will help the users to find various ways to export data for subsequent processing. For this example, the users should select "Component Groups" with Cu(2+) as the Data Object. Select Obs × Variables as the way to display Cu(2+) data, and select Cu(2+) (note the later one means the free Cu²⁺ species) as the interested species to be exported. If the users are not familiar with those processes, they may refer to the tutorials of MINEQL+.
- (5) Then click View to see the results displayed in MINEQL+'s output manager. The values for Cu(2+) are displayed in various units (mole/L, Log C, and %). The values of our ultimate interest is its log C. You may find that the number of rows of the table below is equal to that of the Field Data file.

OBS	SPECIESID	NAME	TYPE	CON
1	30	Cu(2+)	1	2.04
2	30	Cu(2+)	1	8.31
3	30	Cu(2+)	1	2.04
4	30	Cu(2+)	1	8.12
5	30	Cu(2+)	1	0.000
6	30	Cu(2+)	1	0.000
7	30	Cu(2+)	1	0.0
8	30	Cu(2+)	1	0.31
9	30	Cu(2+)	1	2.08
10	30	Cu(2+)	1	2.01
11	30	Cu(2+)	1	2.04
12	30	Cu(2+)	1	8.12
13	30	Cu(2+)	1	0.000
14	30	Cu(2+)	1	0.000
15	30	Cu(2+)	1	0.00
16	30	Cu(2+)	1	8.50
17	30	Cu(2+)	1	2.00
18	30	Cu(2+)	1	8.50
19	30	Cu(2+)	1	2.08
20	30	Cu(2+)	1	8.3
21	30	Cu(2+)	1	0.00
22	30	Cu(2+)	1	0.000
23	30	Cu(2+)	1	0.00
24	30	Cu(2+)	1	2.03
25	30	Cu(2+)	1	8.42
26	30	Cu(2+)	1	1.25
27	30	Cu(2+)	1	7.54
28	30	Cu(2+)	1	1.98
29	30	Cu(2+)	1	8.07
30	30	Cu(2+)	1	0.000

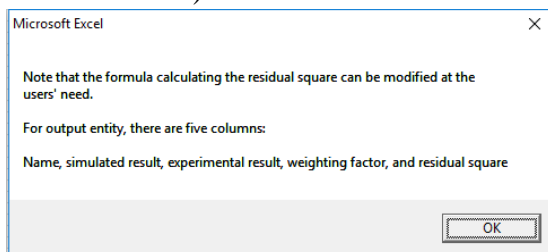
Click Col Xtract to extract the NAME and Log C as the two columns to be saved to the temporary txt file (i.e. chem1). Then only two columns remained.

	NAME	LOGC
1	Cu(2+)	-5.69
2	Cu(2+)	-5.08
3	Cu(2+)	-4.69
4	Cu(2+)	-4.09
5	Cu(2+)	-3.7
6	Cu(2+)	-3.1
7	Cu(2+)	-2.71
8	Cu(2+)	-6.08
9	Cu(2+)	-5.68
10	Cu(2+)	-5.08
11	Cu(2+)	-4.69
12	Cu(2+)	-4.09
13	Cu(2+)	-3.7
14	Cu(2+)	-3.1
15	Cu(2+)	-2.7
16	Cu(2+)	-6.07
17	Cu(2+)	-5.68
18	Cu(2+)	-5.07
19	Cu(2+)	-4.68
20	Cu(2+)	-4.08
21	Cu(2+)	-3.69
22	Cu(2+)	-3.09
23	Cu(2+)	-2.701
24	Cu(2+)	-6.692
25	Cu(2+)	-6.192
26	Cu(2+)	-5.902
27	Cu(2+)	-5.122
28	Cu(2+)	-4.702
29	Cu(2+)	-4.093
30	Cu(2+)	-3.703

It is convenient to save (overwrite) those data to the temporary file that was created previously named “chem1”. At this point, MINFIT already has everything needed to perform calibrations and to find the set of fitting parameters that give the best overall fitting of the experimental results.

Part 4. Parameter calibration in MINFIT

- (1) Turn back to the “Problem” tab and click “Parameter Calibration”. MINFIT was programmed to extract the entries of the temporary files, “chem1” in this example, and to save them into MINFIT’s “MINEQL output” tab. Those data are then transferred to the “Calibration” tab for processing. A popup box tells the users about the format of data in the “Calibration” tab, but the first row of that tab contains all the explanatory information. It also reminds the users that the formula calculating the residual square can be modified at the users’ need in case they want to process the raw output results from MINEQL+ prior to fit (e.g., fit a ratio of two concentrations).



- (2) After clicking OK in the last pop-up box, thousands of calculations are executed in the “Calibration” Tab for the residual sum of squares. After the calculations were done, a popup box will ask which method the user is using for the current round of search. Type in 1 for this example. This selection will be recorded in the “Summary” tab.

Microsoft Excel

What calculation method are you using?

type 1 for grid search, 2 for randomized search

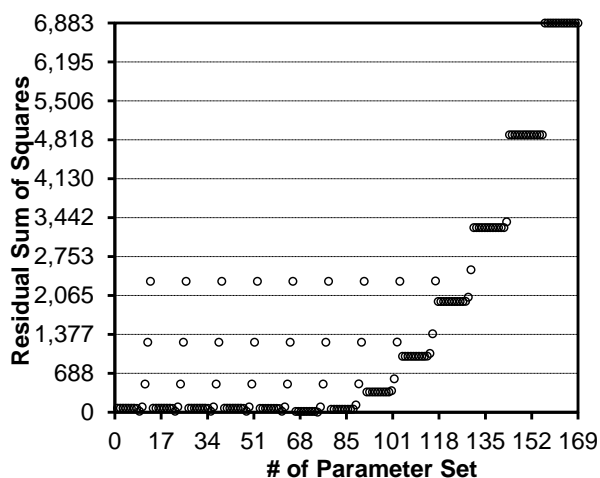
OK

Cancel

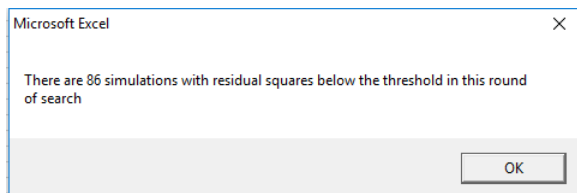
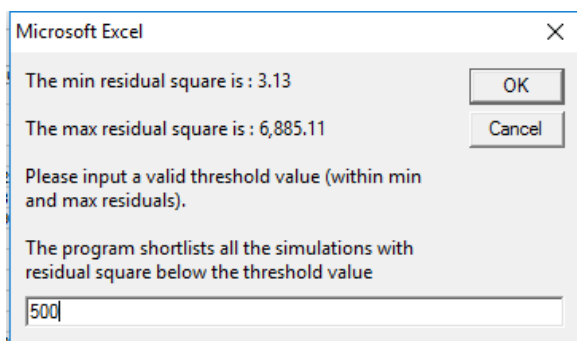
- (3) MINFIT automatically picks out the optimal solution in the current round of search and pastes them together with the search parameters previously defined into a data block in the “Summary” tab. Unless the users click “Clear Summary”, there is a hidden counter in MINFIT that will automatically paste the summary from each round search from top to bottom so the users can keep track of the fitting progress.

CuL(2-)	CuHL(-)		Fitting Parameters	1
-5	-5		Lower Bound (L)	
20	20		Higher Bound (H)	
2	2		Step Length (S)	
min residual	3		Equidistant Grid Search	
1st parameter	2nd parameter	3rd parameter		
5	11			

- (4) Go back to the “Calibration” tab. The information on this tab is comprehensive and MINFIT designs several features to help users process and visualize the data. The built-in plot in “Calibration” tab help visualize the residual sum of squares for each tested parameter set. In the last search, a total number of 169 parameter sets were calculated and compared with the experimental results.



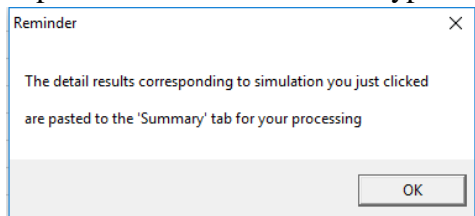
- (5) Click the “Review Residuals” button in the “Calibration” tab. A popup box allows the users to set a threshold value of residual. MINFIT will identify those parameter sets that gave residuals smaller than the threshold value. The popup message highlights the minimal and maximum residual values in the current search, and the plot gives convenient visualization of those results. It is at the users’ discretion to set the threshold values. In this example, enter 500 and see what happens.



- (6) After clicking OK, MINFIT automatically tabulates those results and sorts them from low to high residuals. MINFIT also creates hyperlinks to each parameter set. Below is a partial screenshot.

Residual	Parameter #	CuL(4-)	CuHL(3-)
3	74	5.00	11.00
16	73	5.00	9.00
17	72	5.00	7.00
17	66	5.00	-5.00
17	67	5.00	-3.00
17	68	5.00	-1.00
17	69	5.00	1.00
17	70	5.00	3.00
17	71	5.00	5.00
17	61	3.00	11.00
17	48	1.00	11.00
17	9	-5.00	11.00
17	22	-3.00	11.00
17	35	-1.00	11.00
54	79	7.00	-5.00
54	80	7.00	-3.00
54	81	7.00	-1.00
54	82	7.00	1.00
54	83	7.00	3.00

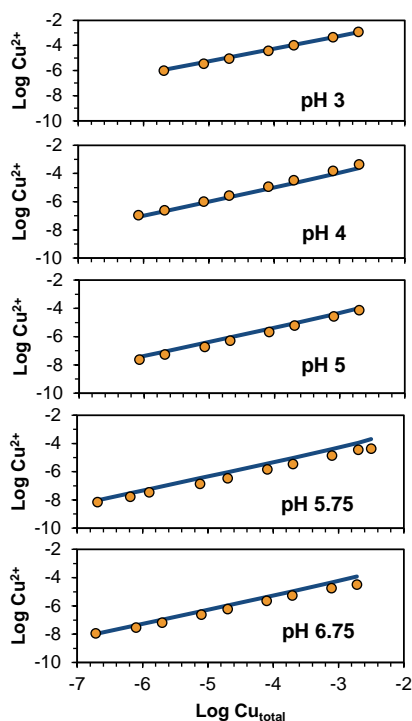
- (7) Those hyperlinks enable convenient review of those calculation in comparison with experimental data. Click the hyperlink of 74. A pop-up box will show



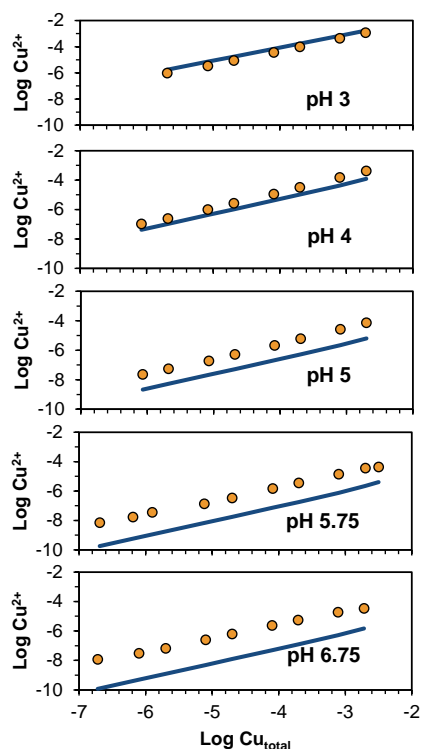
Click OK then the corresponding data block for the #74 parameter set in the “Calibration” tab is pasted to a specific zone in the “Summary” tab.

N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA
NAME	LOGC	Log [Cu ²⁺] measured	Weight	Residual	total Residual	Residual	3	parameter S	pH	Total Cu	Cu _t (2-)	CuHL(-)	
Cu(2+)	-5.944	-6.02	1	0.01	0.01	3.13		74	3	2E-06	5	11	
Cu(2+)	-5.334	-5.46	1	0.02	0.02				3	8.3E-06	5	11	
Cu(2+)	-4.944	-5.05	1	0.01	0.01				3	2E-05	5	11	
Cu(2+)	-4.344	-4.43	1	0.01	0.01				3	8.1E-05	5	11	
Cu(2+)	-3.952	-4.00	1	0.00	0.00				3	0.0002	5	11	
Cu(2+)	-3.348	-3.36	1	0.00	0.00				3	0.00079	5	11	
Cu(2+)	-2.948	-2.92	1	0.00	0.00				3	0.00195	5	11	
Cu(2+)	-7.077	-6.97	1	0.01	0.01				4	8.3E-07	5	11	
Cu(2+)	-6.677	-6.61	1	0.00	0.00				4	2.1E-06	5	11	
Cu(2+)	-6.076	-6.00	1	0.01	0.01				4	8.3E-06	5	11	
Cu(2+)	-5.696	-5.57	1	0.01	0.01				4	2E-05	5	11	
Cu(2+)	-5.084	-4.95	1	0.02	0.02				4	8.1E-05	5	11	
Cu(2+)	-4.69	-4.49	1	0.04	0.04				4	0.0002	5	11	
Cu(2+)	-4.068	-3.82	1	0.06	0.06				4	0.00079	5	11	
Cu(2+)	-3.622	-3.37	1	0.06	0.06				4	0.002	5	11	
Cu(2+)	-7.442	-7.63	1	0.04	0.04				5	8.5E-07	5	11	
Cu(2+)	-7.052	-7.26	1	0.04	0.04				5	2.1E-06	5	11	
Cu(2+)	-6.442	-6.72	1	0.00	0.00				5	8.5E-06	5	11	
Cu(2+)	-6.051	-6.28	1	0.05	0.05				5	2.1E-05	5	11	
Cu(2+)	-5.448	-5.67	1	0.05	0.05				5	8.3E-05	5	11	
Cu(2+)	-5.054	-5.21	1	0.02	0.02				5	0.0002	5	11	
Cu(2+)	-4.428	-4.57	1	0.02	0.02				5	0.00081	5	11	
Cu(2+)	-3.905	-4.13	1	0.02	0.02				5	0.002	5	11	
Cu(2+)	-8.028	-8.16	1	0.02	0.02				5.75	2E-07	5	11	
Cu(2+)	-7.528	-7.78	1	0.06	0.06				5.75	6.5E-07	5	11	
Cu(2+)	-7.238	-7.46	1	0.06	0.06				5.75	1.3E-06	5	11	
Cu(2+)	-6.458	-6.87	1	0.17	0.17				5.75	7.8E-06	5	11	
Cu(2+)	-6.038	-6.47	1	0.19	0.19				5.75	2E-05	5	11	
Cu(2+)	-5.425	-5.84	1	0.17	0.17				5.75	8.1E-05	5	11	
Cu(2+)	-5.03	-5.45	1	0.10	0.10				5.75	0.0002	5	11	
Cu(2+)	-4.406	-4.86	1	0.21	0.21				5.75	0.00079	5	11	
Cu(2+)	-3.952	-4.44	1	0.24	0.24				5.75	0.002	5	11	
Cu(2+)	-3.694	-4.37	1	0.46	0.46				5.75	0.00316	5	11	

- (8) Those data pasted to the “Summary” tab are ready to be plotted to visualize the quality of the fitting. For example, the optimal parameter set (#74) gave the fitting results as below. (The log C on the x axis was not directly displayed in the “Summary” tab shown above, but can be calculated handily from Column Y)



Go back to the “Calibration” tab, and click the hyperlink of parameter set #83 (RSS = 54). The corresponding results are automatically transfer to the “Summary tab” and the plot will be updated as below. Obviously parameter set #83 did a poor job when the pH is closer to neutral. For a specific problem, such graphs only need to be plotted once, as the data they refer to can be automatically updated by clicking the hyperlinks in the “Calibration” tab.



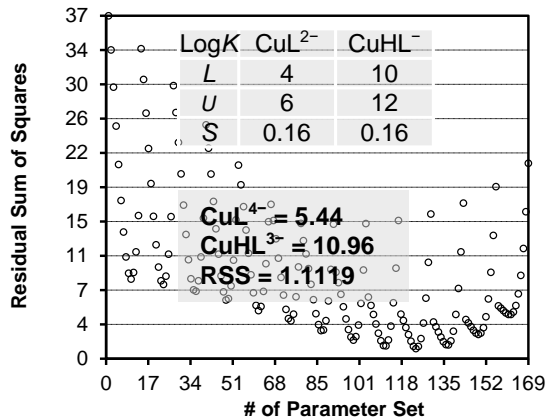
The users can take a detailed look at the results generated by any of the parameters. The users can also reset the threshold value at any time by click the “Review Residuals” button, if they want to examine broader or narrower ranges of results.

Part 5. Iterative search to narrow down

- (1) The last round of search returned 5 and 11 for the two log K respectively as the parameter set that gave the minimal residual (3.14). For the next round of Exhaustive Grid Search. The users may narrow down to a range that is equal to the step length of the precedent search. Set the step length as 0.16 to constrain the total run number below 8,000.

Number of Fitting Parameters (f)		2	
CuL(2-)	CuHL(-)		Fitting Parameters
4	4		Lower Bound (L)
6	6		Higher Bound (H)
0.16	0.16		Step Length (S)
13	13	1	# of Grid (G)
		# of Parameter Set (p)	169
		# of runs in current MINEQL (r)	7,098

- (2) Follow same procedures above to generate new field data, run MINEQL+ and execute parameter calibration. The new plot in the “Calibration” tab will be updated as below (the search parameters and results are manually included for reference).

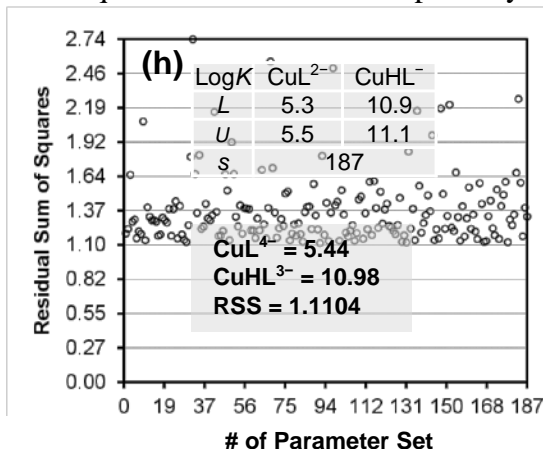


- (3) The last Exhaustive Grid Search already pinpointed the optimal solutions, as the RSS is already so small and visual check of the plots indicated very good fit. The users may want to double check if any better fit might be achieved by randomly searching the ranges neighboring domains. Go back to the “Problem” tab, and edit the table for a Randomized Search.

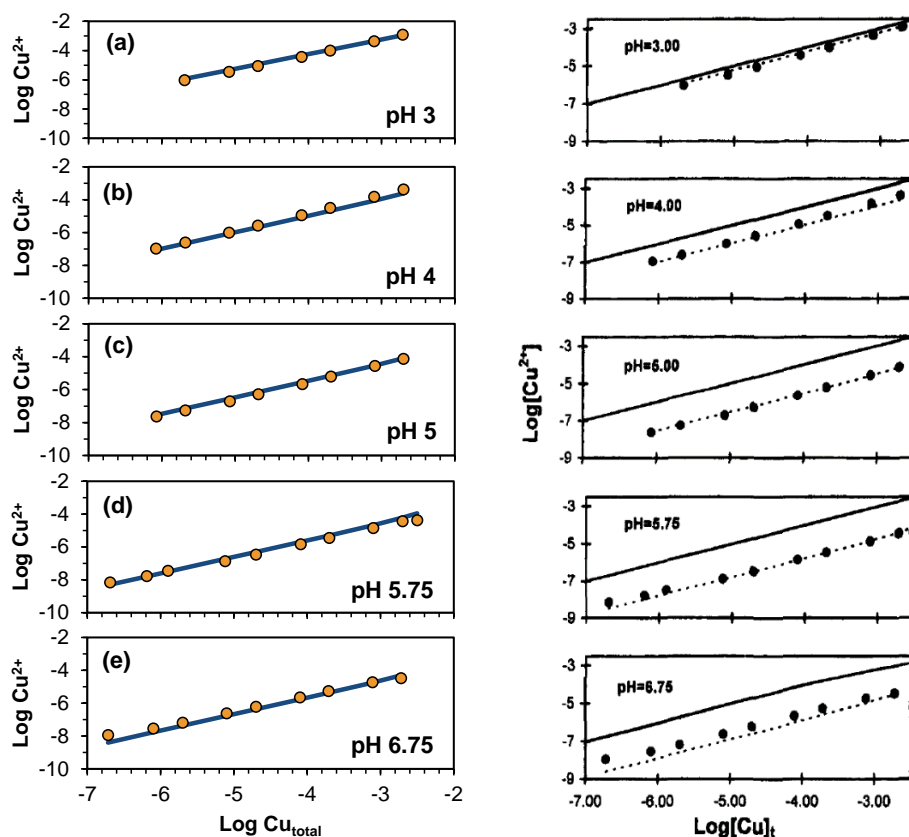
Number of Fitting Parameters (f)		2	
CuL(2-)	CuHL(-)		Fitting Parameters
5.3	10.9		Lower Bound (L)
5.5	11.1		Higher Bound (H)
0.012	0.02		Step Length (S)
17	11	1	# of Grid (G)
		# of Parameter Set (p)	187
		# of runs in current MINEQL (r)	7,854

Note that the lower and higher bounds are only entered to provide the mean and standard deviation of a normal distribution in the Randomized Search. The step lengths were entered only to allow MINFIT to calculate the total number of parameter sets (p), which is needed in generating the random numbers.

- (4) Click “Create Field Data to MINEQL” and select “Randomized Search”. Follow the same steps as before. Normal distributed random numbers will be saved to the “Field Data” file.
- (5) Follow the same steps described above and examine the results in the “Calibration” tab. Not surprisingly, a vast majority of results fall surrounding the optimal solution. The lower boundary in the plot visualizes the lowest residual that optimizing the three equilibrium constants can possibly achieve.





Although a slightly lower residual (1.1104 compared with 1.1119 in the last round of Grid Search) is achieved in the current Randomized Search, it merely depends on how precise the users want to report those values (i.e., how the values would be rounded off). Use the “Review Residual” button and click the hyperlink of the optimal parameter set to generate the final plot as below. The right hand side plot is from Giammar and Dzombak¹, in which they used FITEQL to fit the data (Figure 2 in their paper, the dotted lines are their model predictions). It looks that MINFIT obtained better results than FITEQL did.

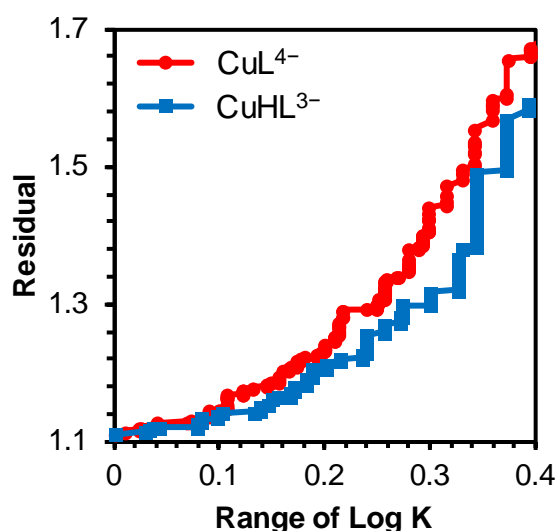


Part 6. Sensitivity analysis and final review

- (1) The review table generated upon clicking “Review Residual” in the “Calibration” tab can also enable straightforward analysis of the sensitivity of the overall fitting to the individual fitting parameter. It is recommended to do sensitivity analysis using the search results which have a large number of trials surrounding the optimal solution, such as the last Randomized Search described above. One can plot the range of each fitting parameter from the very top (the lowest residual) to a certain cutoff residual level as a function of the residual from low to high. The range of each log K can be calculated handily in Excel as below.

S9		:	  f_x		=MAX(Q\$2:Q9)-MIN(Q\$2:Q9)	
	O	P	Q	R	S	T
1	Residual	parameter S	CuL(2-)	CuHL(-)	Range of LogK CuL(2-)	Range of LogK CuHL(-)
2	1.110835	91	5.42	10.37	0.00	0.00
3	1.11543	131	5.43	11.00	0.01	0.03
4	1.118164	178	5.41	10.37	0.02	0.03
5	1.119112	29	5.41	11.01	0.02	0.04
6	1.119643	167	5.41	11.01	0.02	0.04
7	1.120713	129	5.43	11.01	0.03	0.04
8	1.12115	83	5.43	10.34	0.03	0.08
9	1.125889	95	5.39	11.00	0.04	0.08
10	1.126458	168	5.39	10.38	0.04	0.08
11	1.128339	156	5.43	11.02	0.04	0.08
12	1.128657	107	5.46	10.39	0.07	0.08
13	1.129185	100	5.39	11.00	0.07	0.08
14	1.131089	77	5.44	11.02	0.07	0.08
15	1.132495	10	5.47	10.37	0.08	0.08
16	1.133232	144	5.41	10.34	0.08	0.08
17	1.134087	135	5.40	11.03	0.08	0.10
18	1.134401	49	5.39	11.02	0.08	0.10
19	1.136605	28	5.48	10.36	0.09	0.10
20	1.142574	164	5.42	11.04	0.09	0.10
21	1.143573	174	5.45	10.31	0.09	0.13
22	1.145223	111	5.43	11.04	0.09	0.14
23	1.146882	66	5.38	11.03	0.10	0.14
24	1.147264	146	5.39	10.35	0.10	0.14
25	1.147299	35	5.40	10.34	0.11	0.14

(2) Plot column O (as y axis) and column S, T (as x axis) and generate figures below.



For the Cu-pyromellitic complexation model, departing from the optimal solution (residual equal to 1.1108), those less optimal solutions (up to residual equal to 1.6) can allow the both the log K for CuL^{2-} and the log K for CuHL^- to vary in a range of 0.4, indicating that the overall goodness of fit is equally sensitive to the two equilibrium constants. Equivalently, it could be interpreted that varying the log K of both reaction departing from the optimal values (increasing x axis) results in similar extent of increase of the residual (y axis).

- (3) The “Summary” tab recorded all the key information regarding the progress of the parameter estimation. The Grid Search method is reproducible but Randomized Search may give different results each time.

CuL(2-)	CuHL(-)		Fitting Parameters	1
-5	-5		Lower Bound (L)	
20	20		Higher Bound (H)	
2	2		Step Length (S)	
min residual	3		Equidistant Grid Search	
1st parameter	2nd parameter	3rd parameter		
5	11			
CuL(2-)	CuHL(-)		Fitting Parameters	2
4	4		Lower Bound (L)	
6	6		Higher Bound (H)	
0.16	0.16		Step Length (S)	
min residual	3		Equidistant Grid Search	
1st parameter	2nd parameter	3rd parameter		
5.44	10.96			
CuL(2-)	CuHL(-)		Fitting Parameters	3
5.3	10.9		Lower Bound (L)	
5.5	11.1		Higher Bound (H)	
0.02	0.012		Step Length (S)	
min residual	3		Randomized Parameter Search	
1st parameter	2nd parameter	3rd parameter		
5.42	10.97			

Example 2. Chromate adsorption to goethite

Problem Description: Mathur and Dzombak compiled the generalized double layer model dataset for surface complexation reactions on goethite for a variety of cations and anions.² They used FITEQL to simulate the adsorption equilibrium data from multiple independent peer-reviewed publications and reported intrinsic equilibrium constants for zero ionic strength. For simplicity and pragmatic consideration, they employed the monodentate surface complexation reactions and acknowledged that those surface reactions were selected simply for simulating macroscopic adsorption equilibrium rather than reflecting the actual speciation of the surface complexes. The same premise was adopted in the compilation of surface complexation database for hydrous ferric oxide³ and gibbsite⁴. We selected chromate (hexavalent chromium) adsorption to goethite as an example with three fitting parameters to illustrate the capability of MINFIT for parameter estimation. For illustrative purposes, we reproduced Mathur and Dzombak’s model fit to the dataset of Mesuere and Fish⁵ with a total chromate concentration of 0.2 mM and 1.8 g/L goethite at 0.1 M ionic strength.

pH	Measured Adsorbed Cr (%)
4.00	95.68
4.50	94.95
4.96	93.33
5.49	91.17
6.01	87.66
5.99	85.23
6.39	80.90
6.50	76.85
6.85	69.19
7.02	64.68
7.32	53.51
7.69	40.09
8.00	30.81
8.48	17.84
8.92	10.81
9.52	4.32
10.48	0.09

The data were digitalized from the publication of Mesuere and Fish⁵ in print. The fitting results using the unified goethite surface complexation database⁶ was provided by Dave Dzombak (personal communication) and are available in the thesis of Mathur.⁶

The aqueous speciation model of Example 2: Chromate adsorption to goethite

Equilibrium Reactions ^a	Log K^0 ^b	Log K^0 ^c
<i>Chromate surface complexation reaction (to be determined)</i>		
$\equiv\text{FeOH} + \text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \equiv\text{FeCrO}_4^- + \text{H}_2\text{O}$	11.87	11.92
$\equiv\text{FeOH} + \text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \equiv\text{FeHCrO}_4 + \text{H}_2\text{O}$	17.19	17.09
$\equiv\text{FeOH} + \text{CrO}_4^{2-} \rightleftharpoons \equiv\text{FeOHCrO}_4^{2-}$	4.42	4.334
<i>Other reactions (fixed)</i>		
$\equiv\text{FeOH} + \text{H}^+ \rightleftharpoons \equiv\text{FeOH}_2^+$		6.93
$\equiv\text{FeOH} \rightleftharpoons \equiv\text{FeO}^- + \text{H}^+$		-9.65
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$		-13.997
$2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$		14.56
$\text{CrO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HCrO}_4^-$		6.51
$\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{CrO}_{4(\text{aq})}$		6.419

^a Generalized double layer model for goethite as developed by Mathur and Dzombak² with a unified specific surface area of 60 m²/g, and site density of 2 sites/nm². The surface protonation/deprotonation reactions as well as the chromate aqueous speciation reactions were also fixed as in Mathur and Dzombak's model. Equilibrium constants are all corresponding to zero ionic strength.

^b Equilibrium constants obtained using MINFIT by fitting the data of Mesuere and Fish⁵ at 0.2 M total chromate and 1.8 g/L goethite at 0.1 M ionic strength.

^c Equilibrium constants obtained by Mathur⁶ using FITEQL. The SOS/DF (no weighting factor or experimental error was considered) was 0.7. The SOS/DF calculated by MINFIT was 0.88. The tiny

difference is probably caused by the error during our digitalization of the graphic data in Mesuere and Fish's original publication.

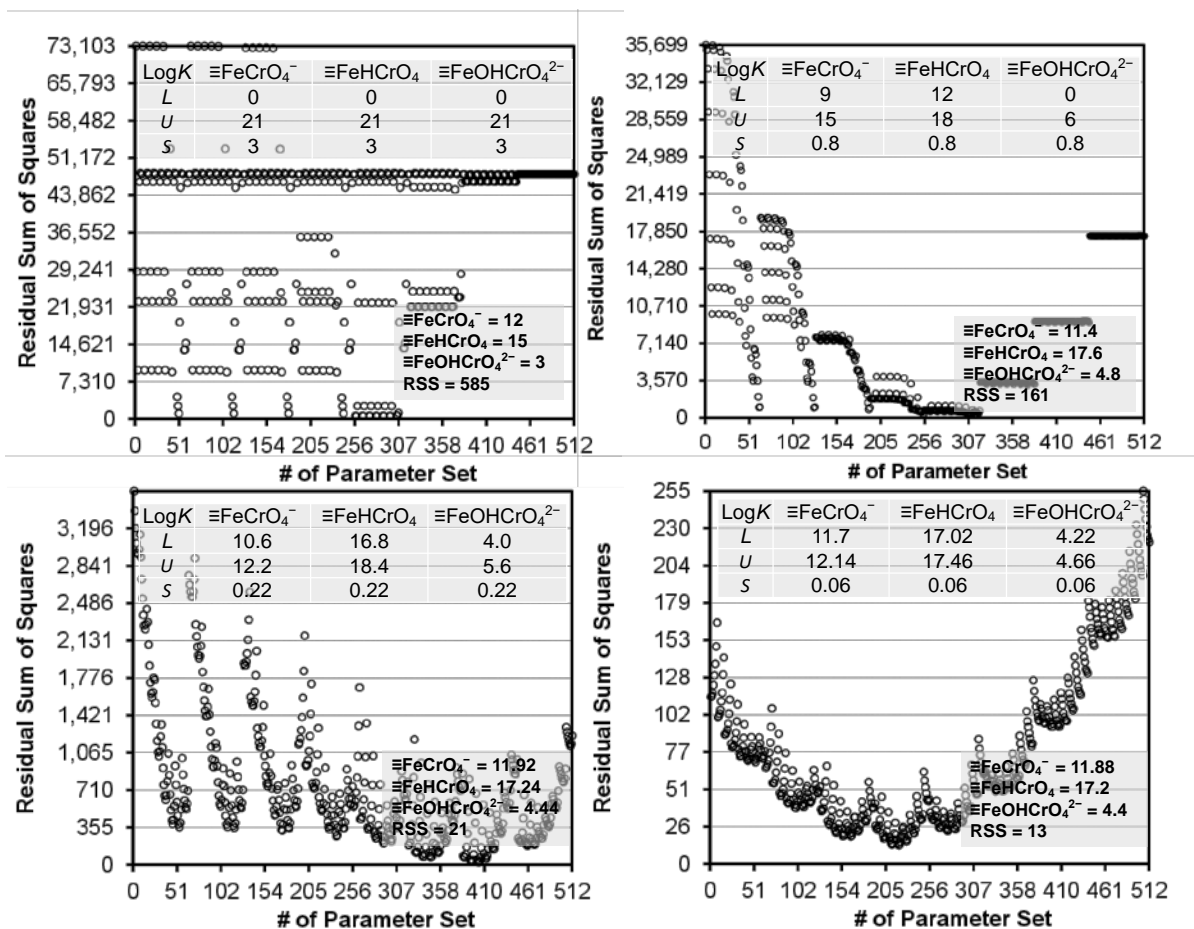
Given that the first example already contains step-by-step explanation, here the illustration is more concise and should be easy enough to follow after reading the first example.

Part 1. Initialize and define the problem in MINFIT

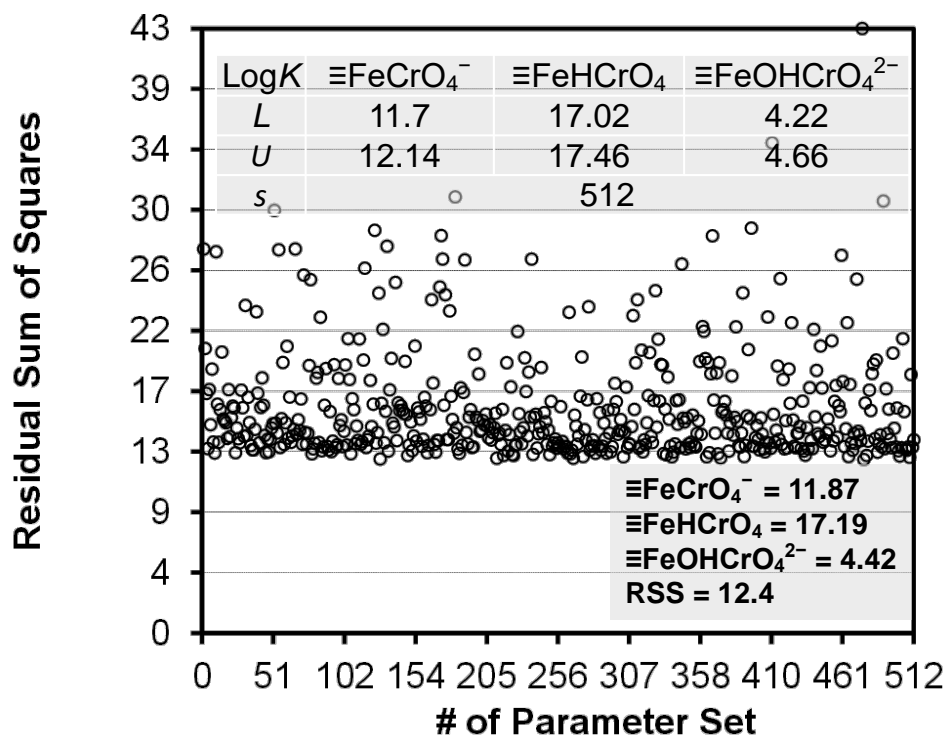
- (1) Set up the problem in MINFIT.

7	Number of Fitting Parameters	3		
8	$\equiv\text{FeCrO}_4^-$	$\equiv\text{FeHCrO}_4$	$\equiv\text{FeOHCrO}_4^{2-}$	Fitting Parameters
9	11.85	17.17	4.37	Lower Bound (L)
10	11.91	17.23	4.43	Higher Bound (H)
11	0.008	0.008	0.008	Step Length (S)
12	8	8	8	# of Grid (G)
13			# of Parameter Set (p)	512
14			# of runs in current MINEQL (r)	8,704
15	# of Input Parameters (i)	1		
16	# of Experiments (e)	17	Number of Dataset to Fit (d')	1
17	pH		% Sorbed	
18	4.00		95.68	
19	4.50		94.95	
20	4.96		93.33	
21	5.49		91.17	
22	6.01		87.66	
23	5.99		85.23	
24	6.39		80.90	
25	6.50		76.85	
26	6.85		69.19	
27	7.02		64.68	
28	7.32		53.51	
29	7.69		40.09	
30	8.00		30.81	
31	8.48		17.84	
32	8.92		10.81	
33	9.52		4.32	
34	10.48		0.09	
35				
36				
37				
38	Weight Table			
39	1			
40	1			

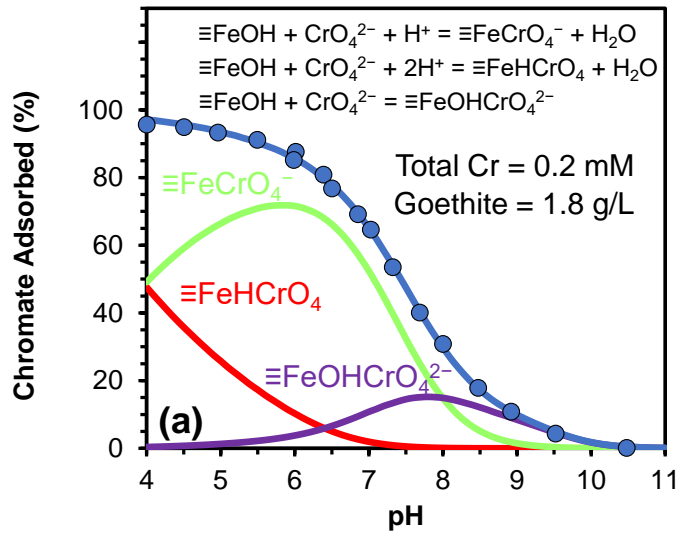
- (2) Perform iterative searches to narrow down to rather small ranges.



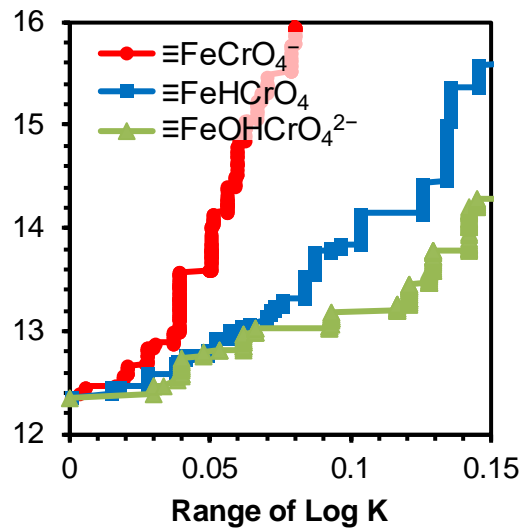
(3) Double check the optimal solution using Randomized Search.



The optimal fit looks like below.



(4) Perform sensitivity analysis.



Departing from the optimal solution (residual equal to 12.4), those less optimal solutions (up to residual equal to 14.2) can allow the log K for $\equiv\text{FeCrO}_4^-$ to vary in a range of 0.05, that for $\equiv\text{FeHCrO}_4$ and $\equiv\text{FeOHCrO}_4^{2-}$ to vary by more than 0.1. It indicates that the overall goodness of fit is most sensitive to the value of log K for $\equiv\text{FeCrO}_4^-$. This is intuitive as the $\equiv\text{FeCrO}_4^-$ species predominantly contributes to the most dramatic range of adsorption edge, and the other two species emerge merely to refine the fits where the edge is flat and not sensitive to the variable (i.e., pH).

Example 3. Sulfate adsorption to ferrihydrite

Problem Description: Using X-ray absorption near edge spectroscopy (XANES), Gu et al. recently quantified the relative contribution and inner sphere (bidentate binuclear as confirmed by EXAFS fitting) and outer sphere surface complexes of sulfate on ferrihydrite surfaces.⁷ They also developed an Extended Triple Layer Model (ETLM) to incorporate the spectroscopically confirmed surface complexes. Comparing with most inverse modeling problems in SCM literature which only involve the macroscopic adsorbate uptake in the object function, this study invoked two datasets to fit ($d = 2$), which are the respective fractions of inner and outer sphere surface complexes out of the total sulfate. The object function to minimize is then the sum of the two sets of residual sum of squares. We benchmark the application of MINFIT with MINEQL+ to solve the optimization problem for the two equilibrium constants (outer and inner sphere surface complexation reactions) by fitting the XANES determined fraction data as a function pH at 0.02 M ionic strength and 1 mM total sulfate loading.

Sulfate adsorption to ferrihydrite

pH	Measured $\equiv\text{FeOH}_2^{+-}\text{HSO}_4^-$ (%)	Measured $(\equiv\text{FeO})_2\text{SO}_2$ (%)
3	57.3	42.6
5	72.4	26.18
6	70.9	12.58
7	35.1	7.69
8	14.2	2.68

The fractions were based on the total sulfate loading and calculated by the macroscopic adsorption percentage and the relative contributions of outer and inner sphere complexations quantified using liner combination fittings of XANES spectra. Details can be found in Gu et al.⁷

The aqueous speciation model of Example 3: Sulfate adsorption to ferrihydrite

Equilibrium Reactions ^a	ψ_0	ψ_β	$\text{Log}K^b$
<i>Sulfate inner- and outer-sphere surface complexation (to be determined)</i>			
$2\equiv\text{FeOH} + 2\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons (\equiv\text{FeO})_2\text{SO}_2 + 2\text{H}_2\text{O}$	0	0	15.5 ^c
$\equiv\text{FeOH} + 2\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \equiv\text{FeOH}_2^{+-}\text{HSO}_4^-$	+1	-1	19.2
<i>Ferrihydrite (de)protonation and electrolyte adsorption (fixed)</i>			
$\equiv\text{FeOH} + \text{H}^+ \rightleftharpoons \equiv\text{FeOH}_2^+$	+1	0	3.7
$\equiv\text{FeOH} \rightleftharpoons \equiv\text{FeO}^- + \text{H}^+$	-1	0	-12.1
$\equiv\text{FeOH} + \text{Na}^+ \rightleftharpoons \equiv\text{FeO}^-\text{Na}^+ + \text{H}^+$	-1	+1	-19.9
$\equiv\text{FeOH} + \text{H}^+ + \text{NO}_3^- \rightleftharpoons \equiv\text{FeOH}_2^+\text{NO}_3^-$	+1	-1	11.9
<i>Aqueous Reactions (fixed)</i>			
$\text{SO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_4^-$	N.A.	N.A.	1.98
$\text{SO}_4^{2-} + \text{Na}^+ \rightleftharpoons \text{NaSO}_4^-$	N.A.	N.A.	0.88
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	N.A.	N.A.	-13.997

^a Extended triple layer model for ferrihydrite as developed by Fukushima and Sverjensky⁸ with a unified specific surface area of 600 m²/g, and site density of 3.8 sites/nm². Capacitance $C_1 = 100 \mu\text{F}/\text{cm}^2$, $C_2 = 20 \mu\text{F}/\text{cm}^2$. For the present model simulation, the total sulfate concentration is 1 mM, ionic strength is 0.02 M as NaNO₃ and ferrihydrite concentration is 2.45 g/L.

^b Equilibrium constants are all corresponding to zero ionic strength. Only the sulfate surface complexation reactions were optimized by fitting the XANES derived surface speciation data. The surface protonation/deprotonation and outer sphere electrolyte complexation reactions were selected based on Fukushi and Sverjensky⁸. More details can be found in Gu et al.⁷

^c For the bidentate surface reaction, the reported Log K here is only applicable for 2.45 g/L ferrihydrite condition. For more information about the how to convert it for other solid loadings, see Wang and Giammar⁹.

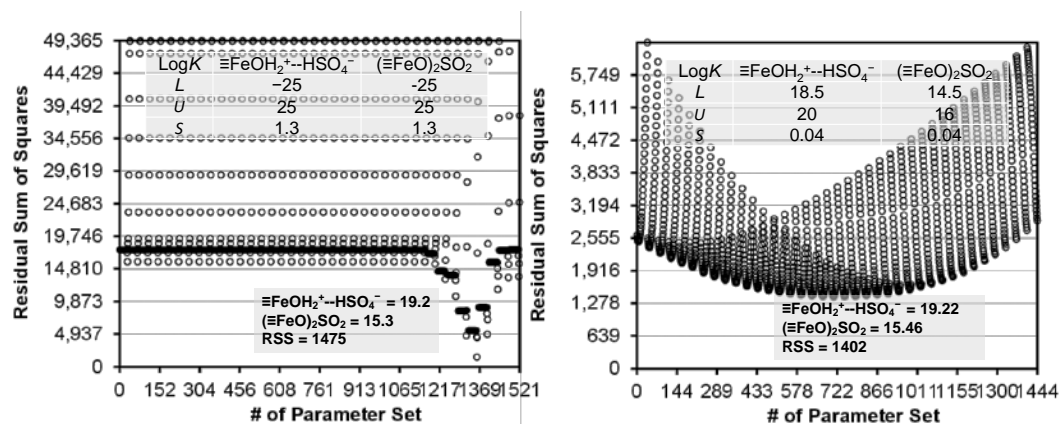
Given that the first example already contains step-by-step explanation, here the illustration is more concise and should be easy enough to follow after reading the first example. This example illustrate the case when d (the number of dataset to fit in each experiment) is larger than one.

Part 1. Initialize and define the problem in MINFIT

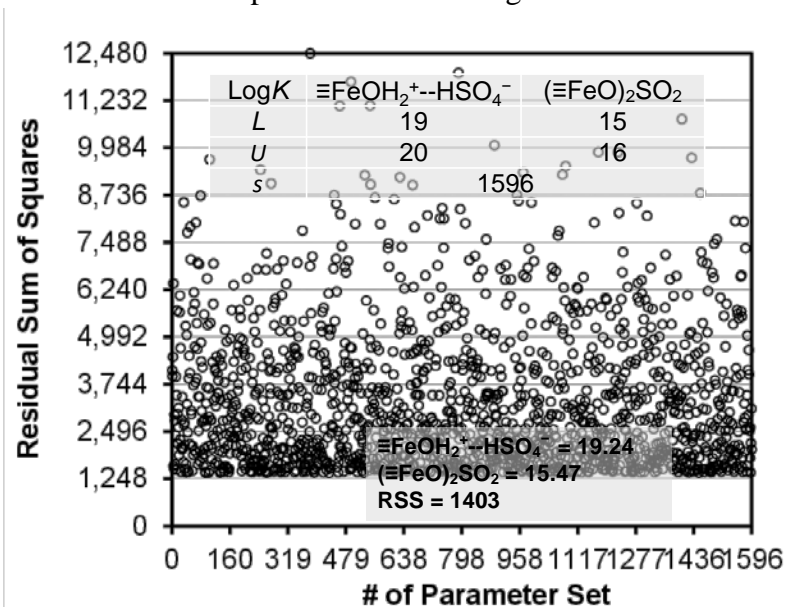
(1) Set up the problem in MINFIT.

	A	B	C	D	E
1	current folder address:	C:\Users\Zimeng\Dropbox\Publications\Journal Paper\2016_Z Wang_MINFIT			
2	Define and Initialize	Create Field Data to MINEQL	Parameter Calibration		
3					
4					
5					
6					
7	Number of Fitting Parameters	2			
8	≡FeOH2+--HSO4- (≡FeO)2SO2			Fitting Parameters	
9	-25	-25		Lower Bound (L)	
10	25	25		Higher Bound (H)	
11	1.3	1.3		Step Length (S)	
12	39	39	1	# of Grid (G)	
13			# of Parameter Set (s)	1,521	
14			# of runs in current MINEQL (t)	7,605	
15	# of Input Parameters (i)	1			
16	# of Experiments (e)	5	of Dataset to Fit in Each Exp	2	
17	pH		(%) ≡FeOH2+--HSO4- (%) (≡FeO)2SO2		
18	3		57.34	42.55	
19	5		72.38	26.18	
20	6		70.88	12.58	
21	7		35.07	7.69	
22	8		14.16	2.68	
23					
24					
25					
26	Weight Table				
27	1	1			
28	1	1			
29	1	1			
30	1	1			
31	1	1			

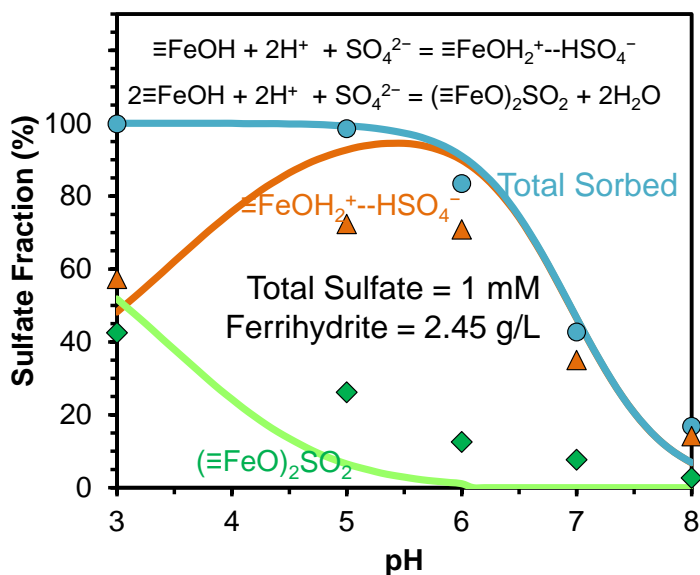
(2) Perform iterative searches to narrow down to rather small ranges.



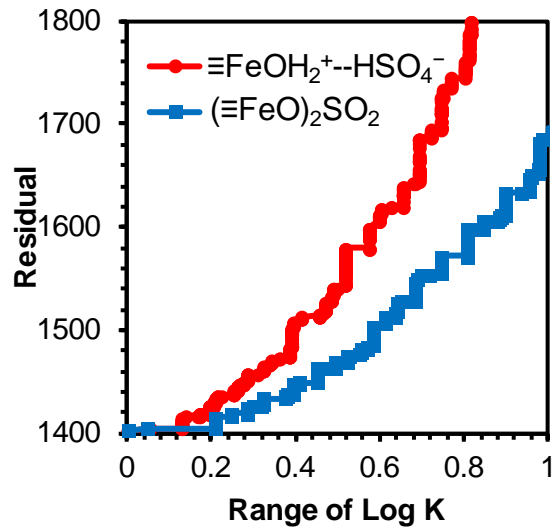
(3) Double check the optimal solution using Randomized Search.



The optimal fit looks like below.



- (4) Perform sensitivity analysis.



For the sulfate-ferrihydrite model (Figure 5c), the fit is slightly more sensitive to the log K for outer sphere reaction. Equivalently, it could be interpreted that varying the log K of the outer sphere reaction departing from the optimal values (increasing x axis) results in more drastic increase of residual.

Additional Features of MINFIT

1. Customization of objective function

In some cases, the data to fit are not directly extractable by MINEQL+'s Output Manager. MINFIT allows the users to edit the formula in the "Calibration" tab to meet such needs. Taking the sulfate-ferrihydrite problem as an example, if we wanted to fit experimentally determined ratio between $\equiv\text{FeOH}_2^+-\text{HSO}_4^-$ and $\equiv\text{FeO})_2\text{SO}_2$, there is a convenient way to enable the calculation in MINFIT.

We may still set $d = 2$ and set up the problem the same as Example 3 except for enter the two column of experimental data both with $[\equiv\text{FeOH}_2^+-\text{HSO}_4^-]/[\equiv\text{FeO})_2\text{SO}_2]$. Then go to the calibration tab to edit the formula of the columns for calculating residuals.

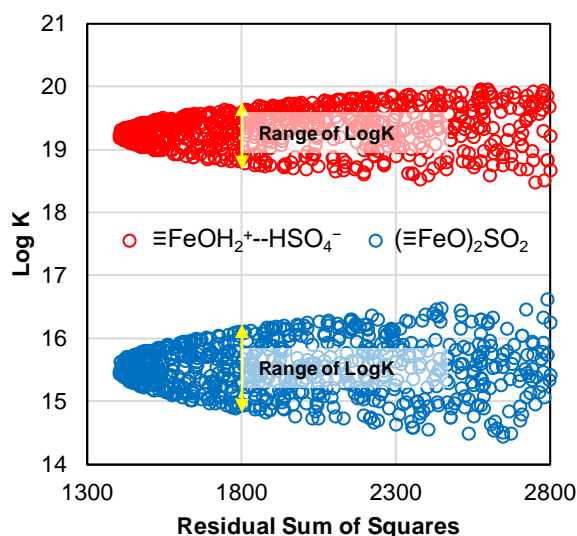
SUM											
=IF(B2="",0,D2*(B2/G2-C2)^2)/2											
	A	B	C	D	E	F	G	H	I	J	K
1	NAME	%TOTAL	Ratio	Weight	Residual	NAME	%TOTAL	Ratio	Weight	Residual	Subtotal Residual
2	SOH-H2SO4	19.4	1.35	1	$(C2^2)/2$	SOH)2-H2SO4	80.6	1.35	1	0.61	1.22
3	SOH-H2SO4	69.8	2.76	1	0.00	SOH)2-H2SO4	25.8	2.76	1	0.00	0.00
4	SOH-H2SO4	54.5	5.64	1	31.92	SOH)2-H2SO4	4	5.64	1	31.92	63.83

2. Alternative ways to visualize parameter sensitivity

In addition to the sensitivity analysis illustrated in Figure 5, we may also visualize the data compiled by "Review Residual" function directly without calculating the range. Still taking the sulfate problem as an example, the "Review Residual" processing gave data below (partial screenshot)

S	T	U	V
Residual	Parameter Set	$\equiv\text{FeOH}_2^+-\text{HSO}_4^-$	$(\equiv\text{FeO})_2\text{SO}_2$
1,403	93	19.24	15.47
1,405	433	19.19	15.43
1,405	101	19.31	15.64
1,406	528	19.25	15.49
1,407	133	19.28	15.63
1,408	260	19.23	15.51
1,408	810	19.20	15.44
1,409	761	19.26	15.53
1,410	927	19.24	15.52
1,411	711	19.25	15.46
1,411	1,423	19.21	15.57
1,413	391	19.19	15.49
1,414	40	19.23	15.44
1,415	857	19.29	15.57
1,417	1,127	19.18	15.39
1,418	615	19.15	15.40
1,418	771	19.15	15.40
1,418	1,098	19.15	15.40
1,418	621	19.24	15.62
1,418	670	19.24	15.62
1,418	265	19.26	15.45
1,419	782	19.20	15.40
1,419	1,073	19.27	15.59
1,419	458	19.34	15.67
1,420	1,269	19.17	15.46
1,420	1,025	19.27	15.65

Then we can simply plot column S with column U and V.



This figure is straightforward visualization of the relative sensitivity for the two log Ks. Both data sets start from the optimal solution and the data set that is more dispersed indicated lower sensitivity. The yellow arrow indicated the range of logK that can be tolerated if the residual increases to a specific level. When the sampled fitting parameter sets are sufficiently dense, the range of logK highlighted by the arrows should be equal to the values calculated as in Figure 5 of the manuscript.

Another more intuitive but more involved method to test parameter sensitivity is to plot RSS versus a specific fitting parameter while keeping all other fitting parameters fixed at their optimal values. Generating such plots requires additional rounds of calculation and cannot be directly exported by processing the “Review Residual” data generated from the precedent randomized (or grid search as long as the grids are sufficiently dense) search. Such calculations can be easily implemented in MINFIT, simply by making the U_n and L_n both equal to the optimal value for the parameter that needs to be fixed.

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