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Method Article

A single-step protocol for closing experimental atom balances

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A B S T R A C T

Molar balances are considered to be closed if they are within 95–105%. It was shown in the companion paper "https://doi.org/10.1016/j.cej.2018.12.113; Chem. Eng. J., 361, 805–811 (2019)" that even this condition can give rise to pronounced deviations in conversion or selectivity data (Heynderickx, 2019). This manuscript offers a very simple a posteriori calculation procedure to address these deviations via simple linear algebra. The specific details of this procedure, called 'CLOBAL', after 'closing the balances', are shared (1) by showing the mathematics behind-the-scene and (2) by showing the specific programming code with an itemized guideline through the code.

Key benefits of proposed procedure CLOBAL script are:

- Physical quantities such as molar flow rates, concentrations or absolute number of moles are updated via a one-step linear procedure to close the corresponding atom balances;
- The presented CLOBAL procedure, is executed in Excel®, which is accessible and practical for every user – no need for special license and the code is provided; and
- Parameter estimation, using treated data, results in smaller confidence intervals and lower residual sum of squares (RSSQ).

A R T I C L E I N F O

Method name: CLOBAL – after 'closing the atom balances', which is exactly what the presented procedure does

Keywords: Closing atom balances, Accuracy, Excel® data sheet

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Specification Table

Subject Area:	Chemical Engineering
More specific subject area:	Fields with experimental outcomes such as molar flow rates, concentrations, moles in organic chemistry experiments, catalysis . . .
Method name:	CLOBAL – after 'closing the atom balances', which is exactly what the presented procedure does
Name and reference of original method:	P. M. Heynderickx, Closing the balance by the CLOBAL procedure: towards more accurate concentration, conversion and selectivity values, https://doi.org/10.1016/j.cej.2018.12.113
Resource availability:	Example of customized procedure is given in file clobal_01.xlsm

Method details

When chemical reactions are performed the corresponding element or atom balances should be always closed [1–5]. For example, if the carbon balance is envisaged in a non-nuclear reaction, the initial number of carbon moles should equal the carbon in the reaction products. Typical acceptable ranges for an atom balance are between 90 % and 110 %. Experimental error is logically invoked to explain why atom balances are not exactly equal to 100 %.

This manuscript describes a very simple and elegant method to set atom balances equal to 100 %. Striking consequence of the given CLOBAL procedure is a more accurate calculation of conversion and selectivity values and a lower residual sum of squares during parameter estimation, accompanied by smaller confidence intervals for the parameters [1].

Consider n measurements of n physical quantities, which 'true' values are called φ_j, j = 1 . . . n. For the sake of example, these quantities are the outlet molar flow rates in a mixture of n compounds, A_j. Each of these compounds A_j has $a_{i,j}$ atoms of type e_i, i = 1 . . . m. Normally the number of compounds exceeds the number of elements taken into account, i.e., m < n. Since there are no nuclear reactions or transformations included, Eq. (1) holds for the true values with $\varphi_{j,0}$ the initial value for quantity φ_j:

$$\sum_{j=1}^{n} a_{ij}\varphi_{j,0} = \sum_{j=1}^{n} a_{ij}\varphi_j \quad i = 1 \ldots m \tag{1}$$

Eq. (1) is an ideal representation, i.e., all the balances for atom type e_i, i = 1 . . . m, are 100 % closed.

In reality this is not the case due to experimental error and, hence, the experimental values for the molar flow rate, absolute number of moles or concentrations do not close Eq. (1). The purpose of this manuscript is to offer a method for small corrections on these physical quantities in order to close the balances 100 %. The order of magnitude of these corrections can be compared to the error related to typical calibration data, as outlined in the companion paper [1], and, if the calibration curve has a high R^2, subsequently small corrections to the concentrations, mol fractions, or derived flowrates, are to be expected with this method. The proposed correction on the physical quantity, $\varphi_{j,c}$ with j = 1 . . . n, should result in a full closure of the m balances, so that Eq. (2) is valid:

$$\sum_{j=1}^{n} a_{ij}\varphi_{j,0} = \sum_{j=1}^{n} a_{ij}\left(\varphi_j + \varphi_{j,c}\right) \quad i = 1 \ldots m \tag{2}$$

Eq. (2) represents m so-called 'fundamental relations' for the n corrections $\varphi_{j,c}$. Hence, n–m additional relations are required to solve for all of their values. These can be found from Eq. (3), which states that the weighted sum of corrections should be minimal, with w_j the weight factor corresponding for correction $\varphi_{j,c}$:

$$R = \sum_{j=1}^{n} w_j\varphi_{j,c}^2 \quad \rightarrow \quad min \tag{3}$$

Eqs. (2) and (3) form the basis for a so-called 'Lagrange multiplicator optimization problem': R needs to be minimized and the solution is subjected to equality constraints, see Eq. (2). The great advantage of the Lagrange multiplicator method is that it allows not to explicitly solve the constraint equations and use them to eliminate extra variables. The complete function, also called the Lagrangian function S [6], with the so-called 'Lagrange multiplicators', $2\cdot\lambda_i$ (i = 1 . . . m), which has to be minimized, reads as Eq. (4):

$$S = \sum_{j=1}^{n} w_j \varphi_{j,c}^2 + \sum_{i=1}^{m} 2\lambda_i \left(\sum_{j=1}^{n} a_{i,j} \varphi_{j,0} - \sum_{j=1}^{n} a_{i,j} \left(\varphi_j + \varphi_{j,c} \right) \right) \quad \rightarrow \quad \min \tag{4}$$

The prefactor '2' for the equality constraint can be added for the sake of elegancy, so that in further calculations the factor 2, as a result of the derivative of the quadratic function (3), can be cancelled out.

Taking the derivative with respect to $\varphi_{j,c}$, gives Eq. (5):

$$\frac{\partial S}{\partial \varphi_{j,c}} = 2\ w_j \varphi_{j,c} - \sum_{i=1}^{m} 2\lambda_i\ a_{i,j} = 0 \quad j = 1 \ldots n \tag{5}$$

From Eq. (5) the optimized corrections for the n flow rates, $\varphi_{j,c}$, are given by Eq. (6):

$$w_j \varphi_{j,c} = \sum_{k=1}^{m} \lambda_k\ a_{k,j} \quad j = 1 \ldots n \tag{6}$$

Eq. (6) contains n relations and m + n unknowns, hence, m additional relations are needed, which can be found in Eq. (2). The subsequent substitution of Eq. (6) in the latter gives Eq. (7):

$$\sum_{j=1}^{n} a_{i,j} \left(\varphi_j - \varphi_{j,0} \right) + \sum_{k=1}^{m} \lambda_k \cdot \sum_{j=1}^{n} a_{k,j} \frac{a_{i,j}}{w_j} = 0 \quad i = 1 \ldots m \tag{7}$$

Eq. (7) represents a set of m linear relations for λ_k, i = 1 . . . m, is found and upon solving, the Lagrange multiplicators are inserted into Eq. (6) to obtain the individual correction for each of the individual n molar flow rates:

$$\varphi_{j,c} = \frac{1}{w_j} \cdot \sum_{k=1}^{m} \lambda_k\ a_{k,j} \quad j = 1 \ldots n \tag{8}$$

The corrected quantities $\varphi_j + \varphi_{j,c}$, for j = 1 . . . n, give complete balances (1). Expressions (7) and (8) are sufficiently detailed to replicate the presented CLOBAL protocol.

The given expressions (7) and (8) can be written in general matrix notation, which will form the basis of the Excel® macro that gives the corrections.

In order to validate the presented methodology, the condensation of benzaldehyde and heptanal, which is an important aldol-type reaction in the production of jasmine aldehyde [7–9], is taken as showcase in the companion paper [1]. There are 5 compounds to be considered: benzaldehyde (C_7H_6O), heptanal ($C_7H_{14}O$), jasmine aldehyde ($C_7H_{14}O$), as desired product, and water (H_2O) and the dimer 2-pentyl-2-nonenal ($C_{14}H_{26}O$) as by-product (n = 5). Three atom types are used: C, O and H (m = 3), so that the stoichiometric matrix, allocating all coefficients $a_{i,j}$, is given by Eq. (9):

$$a = \begin{pmatrix} 7 & 1 & 6 \\ 7 & 1 & 14 \\ 14 & 1 & 18 \\ 0 & 1 & 2 \\ 14 & 1 & 26 \end{pmatrix} \tag{9}$$

The difference in actual value and initial value is given by vector Φ, see Eq. (10), and the correction vector is defined by Eq. (11):

$$(\Phi)_j = \varphi_{j,0} - \varphi_j \quad j = 1 \ldots n \tag{10}$$

Table 1
Excel® code for the CLOBAL procedure.

```
Sub clobal()
' Implementation of CLOBAL procedure for closing experimental balances
Const m_max = 10
Const n_max = 100
Dim m As Integer                                    ' number of atom types
Dim n As Integer                                    ' number of experimental compounds
Dim ndata As Integer                                ' number of data vectors (e.g. at different time points)
Dim data_i_m(n_max, 1) As Double                    ' initial data matrix
Dim datam(n_max, 2) As Double                       ' actual data matrix
Dim atomm(n_max, m_max) As Double                   ' atom matrix
Dim x1, x2, x3, x4, x5, x6, x7 As Variant           ' auxiliary matrices
Dim Rng0, Rng1, Rng2, Rng3 As Range                 ' variable ranges
Dim temp1, temp2 As Double                          ' auxiliary variables
Dim atom_name(m_max) As Variant                     ' atoms in the balances
' Clean the previous (worksheet) data
Worksheets("results").Range("a2:az1000").Clear
' Reading data from 'atom' sheet
ndata = Worksheets("data").Cells(2, 9).Value
m = Worksheets("atom").Cells(3, 2).Value
n = Worksheets("atom").Cells(4, 2).Value
For j = 1 To m
   atom_name(j) = Worksheets("atom").Cells(3, 5 + j).Value
Next
For i = 1 To n
   For j = 1 To m
      atomm(i, j) = Worksheets("atom").Cells(6 + i, j).Value
   Next
Next
' Reading data from 'data' sheet
For i = 1 To n
   data_i_m(i, 1) = Worksheets("data").Cells(2, 1 + i).Value
Next
Set Rng0 = Sheets("data").Range(Sheets("data").Cells(2, 2), Sheets("data").Cells(2, 2 + n - 1))
Set Rng3 = Sheets("data").Range(Sheets("data").Cells(2, 1), Sheets("data").Cells(2 + ndata, 1))
' Feedback of results
Worksheets("results").Cells(3, 1) = "Original balances"
Worksheets("results").Cells(6 + ndata, 1) = "Lagrange multiplicators"
Worksheets("results").Cells(6 + ndata, 3 + m) = "Corrections"
Worksheets("results").Cells(8 + 2 * ndata, 3 + m) = "Corrected data"
For j = 1 To m
   Worksheets("results").Cells(4, 1 + j).Value = atom_name(j)
Next
For i = 1 To n
   Worksheets("results").Cells(9 + 2 * ndata, 3 + m + i).Value = Rng0(i)
Next
For ii = 1 To ndata + 1
   Worksheets("results").Cells(8 + ii + 2 * ndata, 3 + m).Value = Rng3(ii)
Next
' Start procedure
ReDim x3(1 To m, 1 To n)
For j = 1 To m
   For i = 1 To n
      x3(j, i) = atomm(i, j)
   Next
Next
' Loop for complete data treatment
For ii = 1 To ndata
   For i = 1 To n
      datam(i, 1) = Worksheets("data").Cells(2 + ii, 1 + i).Value
      datam(i, 2) = 1 / datam(i, 1)                 ' weight factors
   Next
   ' Processing data
   ReDim x1(1 To n, 1 To 1)
   For i = 1 To n
      x1(i, 1) = data_i_m(i, 1) - datam(i, 1)
   Next
   ReDim x2(1 To n, 1 To m)
   For i = 1 To n
      For j = 1 To m
```

```
70            x2(i, j) = atomm(i, j) / datam(i, 2)
71          Next
72       Next
73       x4 = WorksheetFunction.MMult(x3, x2)
74       x5 = WorksheetFunction.MMult(x3, x1)
75       x6 = WorksheetFunction.MMult(WorksheetFunction.MInverse(x4), x5)
76       x7 = WorksheetFunction.MMult(x2, x6)
77       ' Allocating results
78       Worksheets("results").Cells(4 + ii, 1).Value = ii
79       Worksheets("results").Cells(4 + ii + ndata + 2, 1).Value = ii
80       For j = 1 To m
81          temp1 = 0
82          temp2 = 0
83          Set Rng1 = Sheets("atom").Range(Sheets("atom").Cells(7, j), Sheets("atom").Cells(7 + n - 1, j))
84          Set Rng2 = Sheets("data").Range(Sheets("data").Cells(2 + ii, 2), Sheets("data").Cells(2 + ii, 2 + n - 1))
85          For i = 1 To n
86             temp1 = temp1 + Rng1(i) * Rng0(i)
87             temp2 = temp2 + Rng1(i) * Rng2(i)
88          Next
89          Worksheets("results").Cells(4 + ii, 1 + j).Value = 100 * temp2 / temp1
90       Next
91       For j = 1 To m
92          Worksheets("results").Cells(6 + ndata + ii, 1 + j).Value = x6(j, 1)
93       Next
94       For i = 1 To n
95          Worksheets("results").Cells(6 + ndata + ii, 2 + m + i).Value = x7(i, 1)
96          Worksheets("results").Cells(9 + ii + 2 * ndata, 3 + m + i).Value = datam(i, 1) + x7(i, 1)
97       Next
98    Next
99    End Sub
```

$$\left(\tilde{\Phi}\right)_j = \varphi_{j,c} \quad \mathrm{j} = 1 \ldots \mathrm{n} \tag{11}$$

The solution for the m Lagrange multiplicators is given by Eq. (12) with substitution of matrix $\underline{\underline{v}}$, see Eq. (13):

$$\underline{\lambda} = \left(\underline{a}^T \underline{v}\right)^{-1} \underline{a}^T \underline{\Phi} \tag{12}$$

$$\left(\underline{\underline{v}}\right)_{i,j} = \frac{1}{w_j} \cdot \left(\underline{\underline{a}}\right)_{i,j} \mathrm{i} = 1 \ldots \mathrm{n}, \mathrm{j} = 1 \ldots \mathrm{m} \tag{13}$$

Eq. (12) represents the solution of Eq. (7) in matrix notation with respect to the Lagrange multiplicators.

The corrections $\varphi_{j,c}$ for j = 1 . . . n are given by Eq. (14) in one single step calculation, i.e., no iterations are required:

$$\underline{\tilde{\Phi}} = \underline{v}\ \underline{\lambda} = \underline{v}\left(\underline{a}^T \underline{v}\right)^{-1} \underline{a}^T \underline{\Phi} \tag{14}$$

The corresponding VBA code is given in Table 1. The input requires the number of atom types, m, and the number of compounds, n. The stoichiometric information on the atom types in the individual compounds, such as given by the stoichiometric matrix via Eq. (9), is the input in worksheet 'atom', see Fig. 1. On the third row, the elements are given for further use in the results sheet. In this case the carbon, oxygen and hydrogen balance are evaluated (C, O and H). The code is divided in sections:

- Row 1 to 2: start of the routine;
- Row 3 to 14: declaration of variables;
- Row 15 to 16: removing previous results (avoiding erroneous overlap in data treatment);
- Row 17 to 28: reading input from 'atom' sheet;

	A	B	C	D	E	F	G	H	I	J
1	Application of CLOBAL procedure for data treatment									
2										
3	m	3	number of atom types			C	O	H		
4	n	5	number of compounds							
5										
6	atom data matrix (mxn)									
7	7	1	6							
8	7	1	14							
9	14	1	18							
10	0	1	2							
11	14	1	26							
12										

Fig. 1. Input sheet 'atom' for CLOBAL procedure: information on atom types and input of stoichiometry.

- Row 29 to 34: reading input from 'data' sheet;
- Row 35 to 48: textual setting in the 'result' sheet in order to receive the results;
- Row 49 to 55: CLOBAL procedure starts by transposing the stoichiometric matrix (9);
- Row 56 to 76: all inputted data are treated (ii = 1 . . . ndata) according to Eqs. (10)–(14):
  - x1 contains the elements of vector Φ, see Eq. (10);
  - x2 contains the elements for matrix $\underline{\underline{v}}$, see Eq. (13);
  - x3 is the transposed of matrix $\underline{\underline{a}}$;
  - x4 represents $\underline{\underline{a}}^T\underline{\underline{v}}$;
  - x5 represents $\underline{\underline{a}}^T\Phi$;
  - x6 contains the Lagrange multiplicators, calculated via Eq. (12); and
  - x7 contains the correction on the given physical quantities (in this case, concentrations), calculated via Eq. (14);
- Row 77 to 97: allocation of all the results;
- Row 98: end of the loop over all ndata; and
- Row 99: End of the routine

The data vector consists of ndata+1 rows, having the initial concentration on row 2, see Fig. 2. The value of 'ndata' is automatically read by the program, depending on the input in the worksheet 'data';

	A	B	C	D	E	F	G	H	I	J
1	INPUT DATA									
2	0	1	1	0	0	0		ndata	10	
3	30	0.750578	0.536163	0.198799	0.239414	0.106269				
4	60	0.69623	0.423095	0.305355	0.348544	0.113548				
5	90	0.586689	0.363708	0.396262	0.472754	0.132847				
6	120	0.545978	0.234379	0.366614	0.646785	0.160469				
7	150	0.43947	0.172311	0.502952	0.542378	0.194145				
8	180	0.374929	0.175071	0.422961	0.728719	0.169234				
9	210	0.53502	0.13147	0.558416	0.903967	0.166324				
10	240	0.466952	0.108802	0.490465	0.633123	0.192152				
11	270	0.483465	0.099653	0.625142	0.589533	0.179079				
12	300	0.430545	0.080074	0.504162	0.727041	0.185473				
13										

Fig. 2. Input sheet 'data' for CLOBAL procedure: experimental data, corresponding to initial conditions in the companion paper [1] (CB,0 = 1 M, CH,0 = 2 M), see Fig. 5.

maximal number of data is n_max, n_max = 1000. The actual concentration values for the n compounds occupy the rows 3 to ndata+2. The first column in worksheet 'data' contains the independent variable, e.g., in this case the minutes at sampling. This can be used for preparation of figures, but for the given procedure it is not required.

Fig. 3 gives the results of the CLOBAL procedure: worksheet 'results' evaluates the original atom balances and feeds this back to the user on rows 3 to ndata+4. The Lagrange multiplicators, calculated via Eq. (12), and the individual corrections, obtained via Eq. (14), are given on rows ndata+6 to 2*ndata +6. The corrected data are given from row 2*ndata+8 to 3*ndata+9 and they are ready for further use, i.e., they are generated as in the input form for sheet 'data'.

As a side note for the weight factors, the author found that the best choice is the inverse of the corresponding response; as indicated on line 60 of the code, see Table 1. This can be altered by the user in case another expression should be more appropriate.

As an example, the result of the proposed procedure is given in Figs. 4–7, from which a clear overall decrease in data spread is observable. It has to be mentioned that some points might not show any improvement, such as the point (0.30 M; 0.35 M) in Fig. 5 or the point (0.035 M; 0.024 M) in Fig. 7. This

	A	B	C	D	E	F	G	H	I	J	K	L
1	RESULTS CLOBAL procedure											
2												
3	Original balances											
4		C	O	H								
5	1	94.84383	91.56113	94.14977								
6	2	97.85648	94.33858	96.23211								
7	3	100.4308	97.613	100.7215								
8	4	91.72616	97.71127	93.10998								
9	5	100.2987	92.56278	101.1742								
10	6	86.7194	93.54562	90.85683								
11	7	105.7985	114.7599	106.1727								
12	8	97.04945	94.57473	97.07759								
13	9	109.578	98.84357	106.918								
14	10	94.49442	96.36472	95.27798								
15												
16	Lagrange multiplicators					Corrections						
17	1	-0.02523	0.227457	0.004632		0.059042	0.062042	-0.00842	0.056674	-0.00056		
18	2	-0.02946	0.153346	0.011821		0.012563	0.047647	-0.01415	0.061688	0.005478		
19	3	-0.00171	0.088885	-0.00505		0.027341	0.00226	-0.01029	0.037247	-0.00882		
20	4	0.025563	-0.06717	-0.00812		0.034422	-0.00045	0.052987	-0.05395	0.012767		
21	5	0.00123	0.242536	-0.01569		0.068995	0.005421	-0.01142	0.114524	-0.02878		
22	6	0.069753	0.02029	-0.04159		0.097117	-0.0129	0.104993	-0.04583	-0.0143		
23	7	0.006309	-0.22452	0.005965		-0.07734	-0.01273	-0.01609	-0.19217	0.003145		
24	8	-0.0024	0.100375	-0.00251		0.031995	0.005268	0.010588	0.060369	0.000286		
25	9	-0.04497	0.173929	0.017267		-0.01803	0.01005	-0.09058	0.122896	-0.00121		
26	10	0.012711	0.017739	-0.0068		0.028371	0.000919	0.036922	0.003005	0.003489		
27												
28						Corrected data						
29						0	1	1	0	0	0	
30						30	0.809619	0.598205	0.190381	0.296088	0.105707	
31						60	0.708792	0.470742	0.291208	0.410233	0.119025	
32						90	0.61403	0.365968	0.38597	0.510001	0.124031	
33						120	0.5804	0.233928	0.4196	0.592836	0.173236	
34						150	0.508464	0.177731	0.491536	0.656902	0.165366	
35						180	0.472046	0.162171	0.527954	0.682891	0.154938	
36						210	0.457675	0.118739	0.542325	0.711793	0.169468	
37						240	0.498947	0.11407	0.501053	0.693491	0.192438	
38						270	0.465439	0.109703	0.534561	0.712429	0.177868	
39						300	0.458916	0.080992	0.541084	0.730046	0.188962	
40												

Fig. 3. Results sheet 'results' for CLOBAL procedure, corresponding to initial conditions in the companion paper [1] (CB,0 = 1 M, CH,0 = 2 M), see Fig. 5.

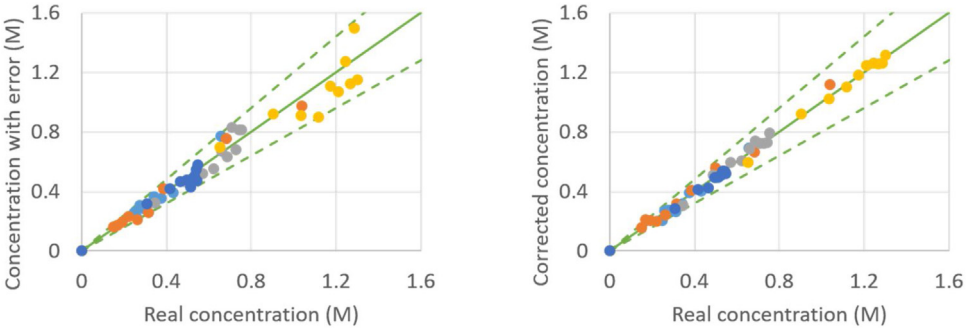

Fig. 4. Concentration with average 10 % error (left) and concentration after CLOBAL procedure (right) versus real concentration. (●) B (benzaldehyde), (●) H (heptanal), (●) J (jasmin aldehyde), (●) W (water), (●) D (2-pentylhept-2-enal) with CB,0 = 1.0 M, CH,0 = 2.0 M, others = 0.0 M [1]. Full green line is the first bisector; dashed lines represent ±20 error.

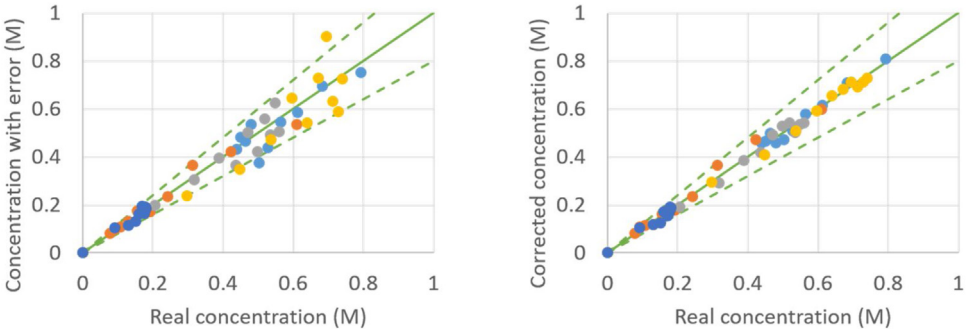

Fig. 5. Concentration with average 10 % error (left) and concentration after CLOBAL procedure (right) versus real concentration. (●) B (benzaldehyde), (●) H (heptanal), (●) J (jasmin aldehyde), (●) W (water), (●) D (2-pentylhept-2-enal) with CB,0 = 1.0 M, CH,0 = 1.0 M, others = 0.0 M [1]. Full green line is the first bisector; dashed lines represent ±20 error.

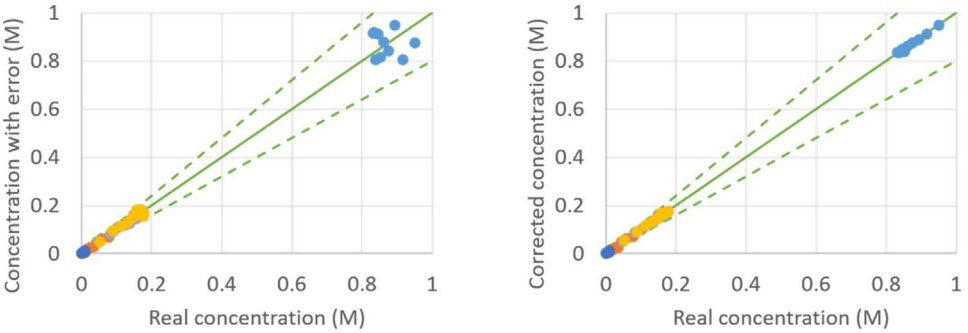

Fig. 6. Concentration with average 10 % error (left) and concentration after CLOBAL procedure (right) versus real concentration. (●) B (benzaldehyde), (●) H (heptanal), (●) J (jasmin aldehyde), (●) W (water), (●) D (2-pentylhept-2-enal) with CB,0 = 1.0 M, CH,0 = 0.2 M, others = 0.0 M [1]. Full green line is the first bisector; dashed lines represent ±20 error.

is purely a coincidence: when the in silico random error is applied a second time [10] and the CLOBAL procedure is subsequently applied, the balances are still closed, but the small variations are somewhat different due to the different randomized error; this time resulting in a visible improvement of the point of interest. It was shown in the companion paper [1] that parameter estimation via ODRpack

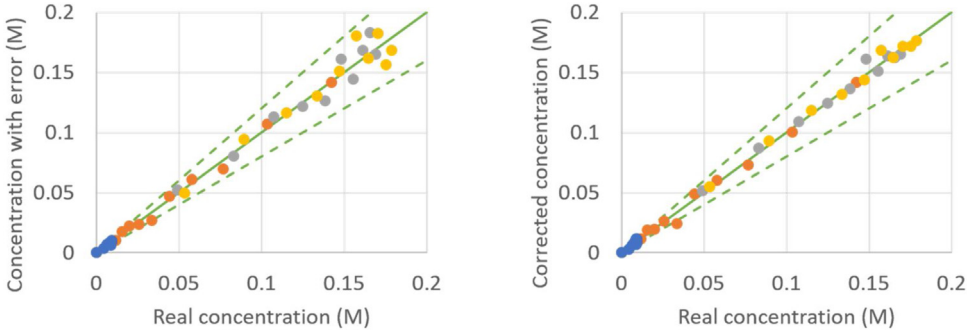

Fig. 7. Concentration with average 10 % error (top) and concentration after CLOBAL procedure (bottom) versus real concentration: zoom of Fig. 6 for concentration range 0 to 0.20 M.

[11], using treated data, results in smaller confidence intervals and lower residual sum of squares (RSSQ).

Declaration of Competing Interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mex.2020.100781.

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