

## Supplementary information for:

### IUPAC Recommended Experimental Methods and Data Evaluation Procedures for the Determination of Radical Copolymerization Reactivity Ratios from Composition Data.

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#### 1 Singularities in the Meyer-Lowry equation (Eq. 4):

##### Solutions for specific situations:

When  $r_1 + r_2 = 2$  ( $r_1, r_2 \neq 1$ ):

As the sum of  $r_1$  and  $r_2$  approaches 2 from below (from above),  $\delta = \frac{1-r_2}{2-r_1-r_2}$  increases (decreases)

without bound and  $\left(\frac{f_{10}-\delta}{f_1-\delta}\right)$  approaches 1.

$$\lim_{r_1+r_2 \rightarrow 2} \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{f_2}{f_{20}}\right)^\beta \left(\frac{f_{10}-\delta}{f_1-\delta}\right)^\gamma = \lim_{\delta \rightarrow \infty} \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{f_2}{f_{20}}\right)^\beta \left(\frac{f_{10}-\delta}{f_1-\delta}\right)^\gamma = \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{f_2}{f_{20}}\right)^\beta 1^\gamma = \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{f_2}{f_{20}}\right)^\beta$$

$$1 - X = \left(\frac{f_1}{f_{10}}\right)^\alpha \left(\frac{f_2}{f_{20}}\right)^\beta$$

When  $r_1 = 1, r_2 \neq 1$ :

Let  $r_1 = 1 + \epsilon$

$$\begin{aligned}
\ln(1 - X) &= \alpha \ln\left(\frac{f_1}{f_{10}}\right) + \beta \ln\left(\frac{f_2}{f_{20}}\right) + \gamma \ln\left(\frac{f_{10} - \delta}{f_1 - \delta}\right) \\
&= \alpha \ln\left(\frac{f_1}{f_{10}}\right) - \frac{1 + \epsilon}{\epsilon} \ln\left(\frac{f_2}{f_{20}}\right) + \frac{1 - (1 + \epsilon)r_2}{-\epsilon(1 - r_2)} \ln\left(\frac{f_{10} - \frac{1 - r_2}{1 - r_2 - \epsilon}}{f_1 - \frac{1 - r_2}{1 - r_2 - \epsilon}}\right) \\
&= \alpha \ln\left(\frac{f_1}{f_{10}}\right) - \left(1 + \frac{1}{\epsilon}\right) \ln\left(\frac{f_2}{f_{20}}\right) - \frac{1}{\epsilon} \ln\left(\frac{f_{10} - 1 - \frac{\epsilon}{1 - r_2 - \epsilon}}{f_1 - 1 - \frac{\epsilon}{1 - r_2 - \epsilon}}\right) \\
&\quad + \frac{r_2}{(1 - r_2)} \ln\left(\frac{f_{10} - 1 - \frac{\epsilon}{1 - r_2 - \epsilon}}{f_1 - 1 - \frac{\epsilon}{1 - r_2 - \epsilon}}\right) \\
&= \alpha \ln\left(\frac{f_1}{f_{10}}\right) - \ln\left(\frac{f_2}{f_{20}}\right) + \frac{1}{\epsilon} \left( \ln\left(\frac{f_2 + \frac{\epsilon}{1 - r_2 - \epsilon}}{f_{20} + \frac{\epsilon}{1 - r_2 - \epsilon}}\right) - \ln\left(\frac{f_2}{f_{20}}\right) \right) \\
&\quad + \alpha \ln\left(\frac{f_{20} + \frac{\epsilon}{1 - r_2 - \epsilon}}{f_2 + \frac{\epsilon}{1 - r_2 - \epsilon}}\right) \\
&= \alpha \ln\left(\frac{f_1}{f_{10}}\right) - \ln\left(\frac{f_2}{f_{20}}\right) + \frac{1}{\epsilon} \ln\left(\frac{1 - r_2 - \epsilon + \epsilon/f_2}{1 - r_2 - \epsilon + \epsilon/f_{20}}\right) \\
&\quad + \alpha \ln\left(\frac{f_{20} + \frac{\epsilon}{1 - r_2 - \epsilon}}{f_2 + \frac{\epsilon}{1 - r_2 - \epsilon}}\right) \\
&= \alpha \ln\left(\frac{f_1}{f_{10}}\right) - \ln\left(\frac{f_2}{f_{20}}\right) + \frac{1}{\epsilon} \ln\left(\frac{1 - r_2 - \frac{\epsilon(f_2 - 1)}{f_2}}{1 - r_2 - \frac{\epsilon(f_{20} - 1)}{f_{20}}}\right) \\
&\quad + \alpha \ln\left(\frac{f_{20} + \frac{\epsilon}{1 - r_2 - \epsilon}}{f_2 + \frac{\epsilon}{1 - r_2 - \epsilon}}\right) \\
&= \alpha \ln\left(\frac{f_1}{f_{10}}\right) - \ln\left(\frac{f_2}{f_{20}}\right) + \frac{1}{\epsilon} \ln\left(\frac{1 - r_2 + \epsilon \frac{f_1}{f_2}}{1 - r_2 + \epsilon \frac{f_{10}}{f_{20}}}\right) + \alpha \ln\left(\frac{f_{20} + \frac{\epsilon}{1 - r_2 - \epsilon}}{f_2 + \frac{\epsilon}{1 - r_2 - \epsilon}}\right)
\end{aligned}$$

$$\begin{aligned}
\lim_{r_1 \rightarrow 1} \ln(1 - X) &= \lim_{\epsilon \rightarrow 0} \left[ \alpha \ln \left( \frac{f_1}{f_{10}} \right) + \ln \left( \frac{f_{20}}{f_2} \right) + \frac{1}{\epsilon} \ln \left( \frac{1 - r_2 + \epsilon \frac{f_1}{f_2}}{1 - r_2 + \epsilon \frac{f_{10}}{f_{20}}} \right) \right. \\
&\quad \left. + \alpha \ln \left( \frac{f_{20} + \frac{\epsilon}{1 - r_2 - \epsilon}}{f_2 + \frac{\epsilon}{1 - r_2 - \epsilon}} \right) \right] \\
&= \alpha \ln \left( \frac{f_1}{f_{10}} \right) + (\alpha + 1) \ln \left( \frac{f_{20}}{f_2} \right) + \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \ln \left( \frac{1 - r_2 + \epsilon \frac{f_1}{f_2}}{1 - r_2 + \epsilon \frac{f_{10}}{f_{20}}} \right)
\end{aligned}$$

By L'Hôpital's rule:

$$\begin{aligned}
\lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \ln \left( \frac{1 - r_2 + \epsilon \frac{f_1}{f_2}}{1 - r_2 + \epsilon \frac{f_{10}}{f_{20}}} \right) &= \lim_{\epsilon \rightarrow 0} \frac{d}{d\epsilon} \ln \left( \frac{1 - r_2 + \epsilon \frac{f_1}{f_2}}{1 - r_2 + \epsilon \frac{f_{10}}{f_{20}}} \right) \\
&= \lim_{\epsilon \rightarrow 0} \frac{d}{d\epsilon} \left( \ln \left( 1 - r_2 + \epsilon \frac{f_1}{f_2} \right) - \ln \left( 1 - r_2 + \epsilon \frac{f_{10}}{f_{20}} \right) \right) \\
&= \lim_{\epsilon \rightarrow 0} \left( \frac{\frac{f_1}{f_2}}{1 - r_2 + \epsilon \frac{f_1}{f_2}} - \frac{\frac{f_{10}}{f_{20}}}{1 - r_2 + \epsilon \frac{f_{10}}{f_{20}}} \right) = \left( \frac{\frac{f_1}{f_2}}{1 - r_2} - \frac{\frac{f_{10}}{f_{20}}}{1 - r_2} \right) \\
&= \frac{1}{1 - r_2} \left( \frac{f_1}{f_2} - \frac{f_{10}}{f_{20}} \right)
\end{aligned}$$

Hence

$$\begin{aligned}
\lim_{r_1 \rightarrow 1} \ln(1 - X) &= \alpha \ln \left( \frac{f_1}{f_{10}} \right) + (\alpha + 1) \ln \left( \frac{f_{20}}{f_2} \right) + \frac{1}{1 - r_2} \left( \frac{f_1}{f_2} - \frac{f_{10}}{f_{20}} \right) \\
\lim_{r_1 \rightarrow 1} (1 - X) &= \left( \frac{f_1}{f_{10}} \right)^\alpha \left( \frac{f_{20}}{f_2} \right)^{\alpha+1} e^{\frac{1}{1-r_2} \left( \frac{f_1}{f_2} - \frac{f_{10}}{f_{20}} \right)}
\end{aligned}$$

When  $r_2 = 1$ ,  $r_1 \neq 1$ :

$$\lim_{r_2 \rightarrow 1} \ln(1 - X) = \beta \ln \left( \frac{f_2}{f_{20}} \right) + (\beta + 1) \ln \left( \frac{f_{10}}{f_1} \right) + \frac{1}{1 - r_1} \left( \frac{f_2}{f_1} - \frac{f_{20}}{f_{10}} \right)$$

$$\lim_{r_1 \rightarrow 1} (1 - X) = \left(\frac{f_2}{f_{20}}\right)^\beta \left(\frac{f_{10}}{f_1}\right)^{\beta+1} e^{\frac{1}{1-r_1} \left(\frac{f_2}{f_1} - \frac{f_{20}}{f_{10}}\right)}$$

When  $r_1 = r_2 = 1$ :

$$\frac{d \ln(1 - X)}{df_1} = \frac{1}{F_1 - f_1}$$

$$\begin{aligned} \frac{df_1}{d \ln(1 - X)} = F_1 - f_1 &= \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} - f_1 = \frac{f_1^2 + f_1 f_2}{f_1^2 + 2f_1 f_2 + f_2^2} - f_1 \\ &= \frac{f_1(f_1 + f_2)}{(f_1 + f_2)^2} - f_1 = 0 \end{aligned}$$

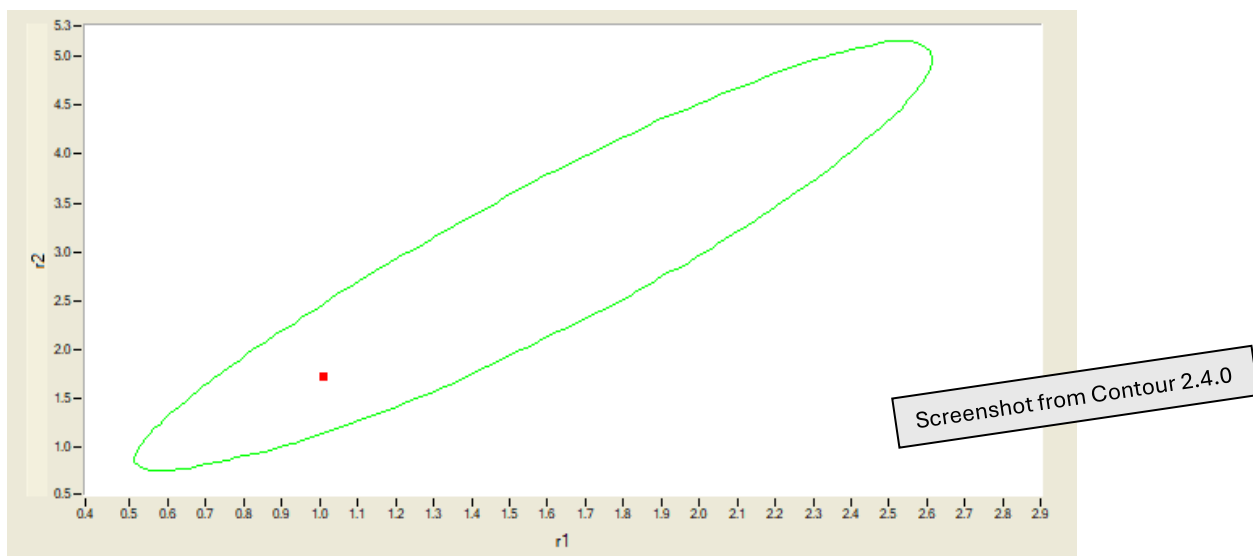
$$f_1 = f_{10}$$

## 2 Indexing issue:

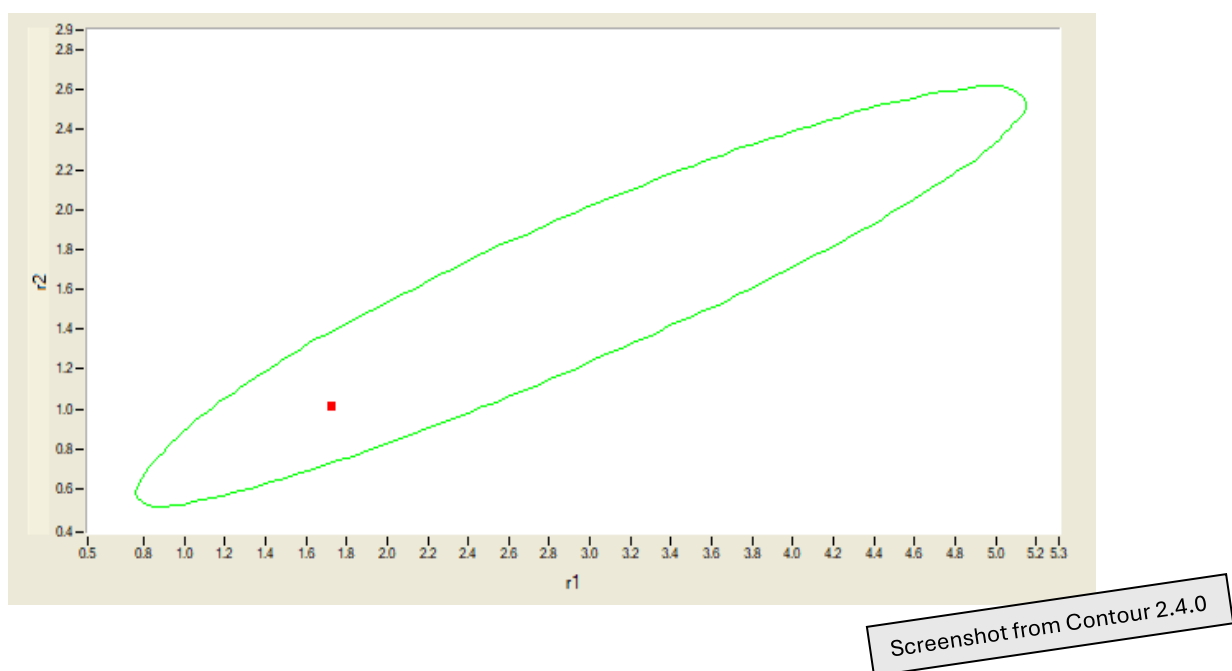
In reference 25, if we switch what is monomer 1 to relabel as monomer 2, but we properly take the errors in  $F$  into account (take the same absolute error in both cases as being 10% from  $F_{VAC}$  values):

Vac-MDO, 10% error in  $F_{VAC}$ :  $r_{MDO}=1.012$ ,  $r_{VAC}= 1.721$

MDO-Vac, error in  $F_{MDO} = \text{abs error } F_{VAC}$ :  $r_{MDO}=1.012$ ,  $r_{VAC}=1.721$



**Figure SI-1** Monomer 1 = MDO, Correct Joint Confidence Intervals as calculated with Contour, compare shape and size to Figure 2 in the main text (approximate JCIs).



**Figure SI-2** Monomer 1 = VAC. Correct Joint Confidence Intervals as calculated with Contour, compare shape and size to Figure 2 in the main text (approximate JCIs).

### 3 Simulation of Fineman-Ross, Kelen-Tüdős and NLLS estimation of reactivity ratios from noisy data (Figure 3):

Figure 3 shows the results of Fineman-Ross (FR), Kelen-Tüdős (KT) and nonlinear least squares (NLLS) estimation of reactivity ratios applied to simulated low conversion copolymer composition data at reactivity ratios of  $r_1 = r_2 = 0.5$  (similar to a styrene-methyl methacrylate copolymerization) and  $r_1 = 10, r_2 = 0.1$  (similar to a methyl acrylate-vinyl acetate copolymerization).

For each pair of reactivity ratios, a set of monomer feed-instantaneous composition ( $f$ - $F$ ) data was generated using the Mayo-Lewis equation (1). The following values were used:

**Table SI-1**

$r_1 = r_2 = 0.5$		$r_1 = 10, r_2 = 0.1$	
$f$	$F$	$f$	$F$
0.2	0.2727	0.04	0.2941
0.8	0.7272	0.21	0.8312
0.33	0.3821	0.33	0.7266
0.67	0.6179	0.67	0.9531

Four data points were generated for each pair of reactivity ratios, consisting of points at  $f_1 = 0.33$  and  $0.67$ , and the Tidwell-Mortimer monomer feeds for each pair of reactivity ratios ( $f_1 = 0.2$  and  $0.8$  for  $r_1 = r_2 = 0.5$ ;  $f_1 = 0.04$  and  $0.21$  for  $r_1 = 10, r_2 = 0.1$ ).

A macro-enabled Excel worksheet (available from SH) was then used to calculate 100 estimates of reactivity ratios using FR, KT or NLLS estimation methods. For each calculation, normally distributed random noise with a standard deviation of 0.01 was applied to the  $F$  values. The  $f$  values were assumed to be free of error. NLLS estimation was iterated 10 times, using the known values of  $r_1$  and  $r_2$  as initial estimates. In addition to the graphs shown in Figure 3, the following statistics were obtained.

**Table SI-2** $r_1 = 0.5, r_2 = 0.5$ 

	FR		KT		NLLS	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
<b>average</b>	0.4991	0.5003	0.4992	0.5008	0.4994	0.5012
<b>std dev</b>	0.0398	0.0486	0.0284	0.0313	0.0277	0.0312
<b>cov(<math>r_1, r_2</math>)</b>	0.00152		0.000468		0.000454	
<b>correlation coefficient</b>	0.791		0.527		0.525	

**Table SI-3** $r_1 = 10, r_2 = 0.1$ 

	FR		KT		NLLS	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
<b>average</b>	10.10	0.1039	9.894	0.0975	9.851	0.0989
<b>std dev</b>	2.952	0.0712	1.760	0.0228	0.538	0.0071
<b>cov(<math>r_1, r_2</math>)</b>	0.205		0.0369		0.00146	
<b>correlation coefficient</b>	0.976		0.919		0.386	

All methods give, on average, results for  $r_1$  and  $r_2$  that are close to the underlying values. However, the scatter of the individual estimates, as measured by the standard deviation, varies depending on the method. Fineman-Ross is consistently less accurate than Kelen-Tüdős and NLLS. While for  $r_1 = r_2 = 0.5$ , there is little difference in accuracy between the KT and NLLS methods for  $r_1 = 10, r_2 = 0.1$ , NLLS gives significantly more accurate estimates of the reactivity ratios.

The Visual Basic code used to generate the estimates of  $r_1$  and  $r_2$  is given below:

```
Option Explicit
Dim r1 As Single
Dim r2 As Single
```

```

Const N As Integer = 4
Const sd As Single = 0.01
Dim f1(N) As Single
Dim BigF1(N) As Single
Dim NoisyBigF1(N) As Single
Dim eps(N) As Single
Dim G(N) As Single
Dim H(N) As Single
Dim SumG As Single
Dim sumH2 As Single
Dim sumH As Single
Dim sumGH As Single
Dim alpha As Single
Dim MinH As Single
Dim MaxH As Single
Dim mu(N) As Single
Dim eta(N) As Single
Dim summu As Single
Dim sumeta As Single
Dim summu2 As Single
Dim sumetamu As Single
Dim r1FR(100) As Single
Dim r2FR(100) As Single
Dim r1KT(100) As Single
Dim r2KT(100) As Single
Dim r1guess As Single
Dim r2guess As Single
Dim BigF1hat(N) As Single
Dim residual(N) As Single
Dim dF1dr1(N) As Single
Dim dF1dr2(N) As Single
Dim A(1, 1) As Single
Dim B(1) As Single
Dim SSR As Single
Dim D As Single
Dim i As Integer
Dim j As Integer
Dim k As Integer

Private Sub CommandButton1_Click()
r1 = Cells(1, 2).Value
r2 = Cells(1, 4).Value
For i = 1 To N
    f1(i) = Cells(3 + i, 1).Value
    BigF1(i) = Cells(3 + i, 2).Value
Next i

For i = 1 To 100
    SumG = 0
    sumH2 = 0
    sumH = 0
    sumGH = 0
    For j = 1 To N
        eps(j) = sd * Application.WorksheetFunction.Norm_S_Inv(Rnd())
        NoisyBigF1(j) = BigF1(j) + eps(j)
        If NoisyBigF1(j) < 0.001 Then NoisyBigF1(j) = 0.001
        If NoisyBigF1(j) > 0.999 Then NoisyBigF1(j) = 0.999
        G(j) = f1(j) * (2 * NoisyBigF1(j) - 1) / (1 - f1(j)) /
NoisyBigF1(j)
        H(j) = f1(j) ^ 2 * (1 - NoisyBigF1(j)) / (1 - f1(j)) ^ 2 /
NoisyBigF1(j)

```



```

SumG = SumG + G(j)
sumH2 = sumH2 + H(j) ^ 2
sumH = sumH + H(j)
sumGH = sumGH + G(j) * H(j)
Next j
MinH = H(1)
MaxH = H(1)
For j = 2 To N
    If H(j) < MinH Then MinH = H(j)
    If H(j) > MaxH Then MaxH = H(j)
Next j
alpha = (MinH * MaxH) ^ 0.5
sumeta = 0
summu2 = 0
summu = 0
sumetamu = 0
For j = 1 To N
    eta(j) = G(j) / (alpha + H(j))
    mu(j) = H(j) / (alpha + H(j))
    sumeta = sumeta + eta(j)
    summu2 = summu2 + mu(j) ^ 2
    summu = summu + mu(j)
    sumetamu = sumetamu + eta(j) * mu(j)
Next j
r1FR(i) = (N * sumGH - SumG * sumH) / (N * sumH2 - sumH ^ 2)
r2FR(i) = -(sumH2 * SumG - sumH * sumGH) / (N * sumH2 - sumH ^ 2)
r1KT(i) = (N * sumetamu - sumeta * summu) / (N * summu2 - summu ^ 2) +
(summu2 * sumeta - summu * sumetamu) / (N * summu2 - summu ^ 2)
r2KT(i) = -alpha * (summu2 * sumeta - summu * sumetamu) / (N * summu2 -
summu ^ 2)
Cells(i + 1, 9).Value = r1FR(i)
Cells(i + 1, 10).Value = r2FR(i)
Cells(i + 1, 11).Value = r1KT(i)
Cells(i + 1, 12).Value = r2KT(i)
'NLLS
r1guess = r1
r2guess = r2
For k = 1 To 10
    A(0, 0) = 0
    A(0, 1) = 0
    A(1, 1) = 0
    B(0) = 0
    B(1) = 0
    SSR = 0
    For j = 1 To N
        BigFlhat(j) = (r1guess * f1(j) ^ 2 + f1(j) * (1 - f1(j))) /
(r1guess * f1(j) ^ 2 + 2 * f1(j) * (1 - f1(j)) + r2guess * (1 - f1(j)) ^ 2)
        residual(j) = NoisyBigFl(j) - BigFlhat(j)
        dF1dr1(j) = (1 - f1(j)) * f1(j) ^ 2 * (r2guess * (1 - f1(j)) +
f1(j)) / (r1guess * f1(j) ^ 2 + 2 * f1(j) * (1 - f1(j)) + r2guess * (1 -
f1(j)) ^ 2) ^ 2
        dF1dr2(j) = -(1 - f1(j)) ^ 2 * f1(j) * (r1guess * f1(j) + (1 -
f1(j))) / (r1guess * f1(j) ^ 2 + 2 * f1(j) * (1 - f1(j)) + r2guess * (1 -
f1(j)) ^ 2) ^ 2
        A(0, 0) = A(0, 0) + dF1dr1(j) ^ 2
        A(0, 1) = A(0, 1) + dF1dr1(j) * dF1dr2(j)
        A(1, 1) = A(1, 1) + dF1dr2(j) ^ 2
        B(0) = B(0) + residual(j) * dF1dr1(j)
        B(1) = B(1) + residual(j) * dF1dr2(j)
        SSR = SSR + residual(j) ^ 2
    Next j

```

```

D = A(1, 1) * A(0, 0) - A(0, 1) ^ 2
r1guess = r1guess + A(1, 1) / D * B(0) - A(0, 1) / D * B(1)
r2guess = r2guess + A(0, 0) / D * B(1) - A(0, 1) / D * B(0)
Next k
Cells(i + 1, 13).Value = r1guess
Cells(i + 1, 14).Value = r2guess
Next i
End Sub

```

## 4 Copolymerization examples

### 4a Simulated dataset for IUPAC method testing

**Table SI-4**  $r_1 = 0.4$  and  $r_2 = 0.6$ , random noise of  $\pm 0.005$  on  $X$  and  $F$  added. Obtained with Contour, estimated errors and error in  $F$  constant.

Theoretical sum of squares: 0.000900, Minimum sum of squares: 0.000063  
95 % confidence limit: 0.000075, 90 % confidence limit: 0.000072  
 $(r_1, r_2) = (0.401, 0.601)$

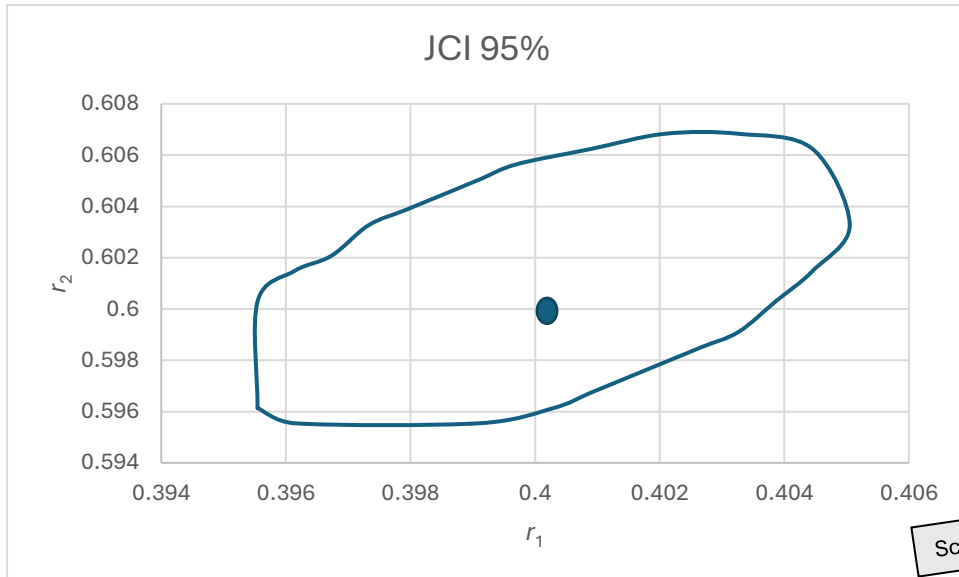
f10	X	F1	F1Calc	delta th.	delta calc	delta %
0.100	0.100	0.139	0.138	0.005	0.00117	0.84
0.100	0.200	0.134	0.135	0.005	-0.00120	-0.90
0.100	0.302	0.134	0.132	0.005	0.00211	1.57
0.100	0.402	0.130	0.129	0.005	0.00031	0.24
0.100	0.502	0.127	0.126	0.005	0.00087	0.69
0.100	0.602	0.121	0.122	0.005	-0.00072	-0.59
0.100	0.702	0.120	0.118	0.005	0.00214	1.78
0.100	0.802	0.115	0.113	0.005	0.00228	1.97
0.100	0.900	0.109	0.108	0.005	0.00174	1.59
0.300	0.098	0.326	0.327	0.005	-0.00108	-0.33
0.300	0.202	0.326	0.326	0.005	0.00017	0.05
0.300	0.299	0.324	0.324	0.005	-0.00082	-0.25
0.300	0.398	0.325	0.323	0.005	0.00184	0.57
0.300	0.502	0.319	0.321	0.005	-0.00218	-0.68
0.300	0.599	0.319	0.319	0.005	-0.00028	-0.09
0.300	0.701	0.317	0.317	0.005	0.00056	0.18
0.300	0.799	0.311	0.314	0.005	-0.00238	-0.77
0.300	0.898	0.309	0.309	0.005	-0.00059	-0.19
0.500	0.100	0.466	0.468	0.005	-0.00193	-0.41
0.500	0.198	0.468	0.469	0.005	-0.00110	-0.23
0.500	0.301	0.472	0.471	0.005	0.00104	0.22
0.500	0.400	0.473	0.472	0.005	0.00069	0.15
0.500	0.499	0.475	0.474	0.005	0.00109	0.23
0.500	0.600	0.476	0.476	0.005	-0.00041	-0.09
0.500	0.702	0.479	0.479	0.005	0.00012	0.03
0.500	0.798	0.482	0.482	0.005	-0.00040	-0.08
0.500	0.900	0.488	0.488	0.005	0.00059	0.12
0.800	0.101	0.700	0.700	0.005	0.00065	0.09
0.800	0.201	0.707	0.706	0.005	0.00121	0.17
0.800	0.302	0.712	0.713	0.005	-0.00072	-0.10
0.800	0.400	0.722	0.720	0.005	0.00160	0.22
0.800	0.500	0.729	0.729	0.005	0.00019	0.03
0.800	0.600	0.736	0.739	0.005	-0.00312	-0.42
0.800	0.698	0.750	0.750	0.005	-0.00028	-0.04
0.800	0.799	0.764	0.764	0.005	-0.00016	-0.02
0.800	0.902	0.780	0.782	0.005	-0.00151	-0.19

av. error 0.447755 %

Error in composition as estimated from fit 0.001365

Error in composition from the estimations in measurements 0.005145

The model provides an adequate fit to the data (95 % probability)



**Figure SI-3** Corresponding 95% joint confidence interval for  $r_1 = 0.4$  and  $r_2 = 0.6$ , random noise of  $\pm 0.005$  on  $X$  and  $F$  added.

#### 4b Experimental dataset APSA-VIM

**Table SI-5** Full APSA-VIM data set with absolute error constant in  $F$  (0.03).

Theoretical sum of squares: 0.027900, Minimum sum of squares: 0.040207  
 95 % confidence limit: 0.048941, 90 % confidence limit: 0.046834  
 $(r1,r2)=(0.397,0.022)$

f10	X	F1	F1Calc	delta th.	delta calc	delta %
0.050	0.040	0.404	0.406	0.030	-0.00183	-0.45
0.050	0.093	0.381	0.376	0.030	0.00452	1.19
0.050	0.209	0.316	0.239	0.030	0.07722	24.44
0.050	0.195	0.282	0.255	0.030	0.02675	9.49
0.050	0.279	0.227	0.179	0.030	0.04779	21.05
0.050	0.434	0.146	0.115	0.030	0.03079	21.09
0.100	0.100	0.458	0.453	0.030	0.00538	1.17
0.100	0.182	0.457	0.431	0.030	0.02581	5.65
0.100	0.194	0.407	0.426	0.030	-0.01917	-4.71
0.100	0.301	0.396	0.332	0.030	0.06422	16.22
0.100	0.389	0.347	0.257	0.030	0.08993	25.92
0.100	0.474	0.235	0.211	0.030	0.02403	10.23
0.300	0.109	0.547	0.524	0.030	0.02314	4.23
0.300	0.168	0.491	0.522	0.030	-0.03101	-6.32
0.300	0.201	0.484	0.521	0.030	-0.03691	-7.63
0.300	0.383	0.486	0.513	0.030	-0.02735	-5.63
0.300	0.456	0.488	0.509	0.030	-0.02109	-4.32
0.300	0.731	0.467	0.410	0.030	0.05660	12.12
0.700	0.068	0.658	0.657	0.030	0.00074	0.11
0.700	0.186	0.654	0.659	0.030	-0.00486	-0.74
0.700	0.274	0.677	0.660	0.030	0.01678	2.48
0.700	0.332	0.642	0.661	0.030	-0.01922	-2.99
0.700	0.482	0.635	0.664	0.030	-0.02927	-4.61
0.700	0.577	0.649	0.667	0.030	-0.01770	-2.73
0.700	0.739	0.658	0.672	0.030	-0.01444	-2.19
0.900	0.130	0.872	0.828	0.030	0.04382	5.02
0.900	0.273	0.856	0.837	0.030	0.01913	2.24
0.900	0.430	0.830	0.848	0.030	-0.01773	-2.14
0.900	0.585	0.915	0.860	0.030	0.05490	6.00
0.900	0.710	0.910	0.871	0.030	0.03860	4.24
0.900	0.820	0.880	0.882	0.030	-0.00230	-0.26
av. error 7.019360 %						

Error in composition as estimated from fit 0.037235  
 Error in composition from the estimations in measurements 0.031017

The model provides an adequate fit to the data (95 % probability)

Screenshot from Contour 2.4.0

Error distribution is not symmetric!  
 Estimated standard deviations are only very crude estimates now.

**$r1 = 0.397 (-0.054 +0.068)$ ,  $r2 = 0.022 (-0.006 +0.007)$**

#### 4-c Recalculation with $f_{10}=0.05$ and $f_{10}=0.1$ taken out:

**Table SI-6** Partial APSA-VIM data set ( $f_{10}=0.05$  and  $f_{10}=0.1$ ) taken out with absolute error constant in  $F$  (0.03).

Theoretical sum of squares: 0.017100, Minimum sum of squares: 0.014163  
 95 % confidence limit: 0.020145, 90 % confidence limit: 0.018562  
 ( $r_1, r_2$ )=(0.420,0.058)

f10	X	F1	F1Calc	delta th.	delta calc	delta %
0.300	0.109	0.547	0.506	0.030	0.04131	7.55
0.300	0.168	0.491	0.503	0.030	-0.01224	-2.49
0.300	0.201	0.484	0.502	0.030	-0.01776	-3.67
0.300	0.383	0.486	0.491	0.030	-0.00544	-1.12
0.300	0.456	0.488	0.486	0.030	0.00241	0.49
0.300	0.731	0.467	0.410	0.030	0.05674	12.15
0.700	0.068	0.658	0.660	0.030	-0.00195	-0.30
0.700	0.186	0.654	0.662	0.030	-0.00753	-1.15
0.700	0.274	0.677	0.663	0.030	0.01414	2.09
0.700	0.332	0.642	0.664	0.030	-0.02184	-3.40
0.700	0.482	0.635	0.667	0.030	-0.03180	-5.01
0.700	0.577	0.649	0.669	0.030	-0.02015	-3.10
0.700	0.739	0.658	0.675	0.030	-0.01661	-2.52
0.900	0.130	0.872	0.833	0.030	0.03860	4.43
0.900	0.273	0.856	0.841	0.030	0.01467	1.71
0.900	0.430	0.830	0.851	0.030	-0.02122	-2.56
0.900	0.585	0.915	0.862	0.030	0.05253	5.74
0.900	0.710	0.910	0.873	0.030	0.03718	4.09
0.900	0.820	0.880	0.883	0.030	-0.00294	-0.33

av. error 3.363824 %

Error in composition as estimated from fit 0.028864  
 Error in composition from the estimations in measurements 0.031716

The model provides an adequate fit to the data (95 % probability)

Error distribution is not symmetric!  
 Estimated standard deviations are only very crude estimates now.

**$r_1 = 0.420 (-0.051 +0.062)$ ,  $r_2 = 0.058 (-0.028 +0.033)$**

Screenshot from Contour 2.4.0

#### 5 Comparison of analysis of $X$ vs $f$ data and the same data converted to $f_0$ - $X$ - $F$ data.

A simulated set of  $X$  vs  $f$  is used with original reactivity ratios of 0.3 and 2 and some random noise added. Initial monomer fraction  $f_{10}=0.4$ . VSSS method with individual point weighting, in both cases with absolute error in  $X$  constant  $\pm 0.005$ , for second case also error in  $f$  of  $\pm 0.005$  assumed, error propagation according to Equation 8 in the paper, leading to variable errors in  $F$ .

**Table SI-7** Simulated set of  $X$  vs  $f$  with original reactivity ratios of 0.3 and 2 and random noise added. Initial monomer fraction  $f_{10}=0.4$ .

$f_{10}$	$f$	$X$	Delta $X$	Delta $f$	$f_{10}$	$X$	$F$	Delta $F$
0.4	0.45	0.246	0.005	0.005	0.4	0.246	0.247	0.01587
0.4	0.5	0.419	0.005	0.005	0.4	0.419	0.261	0.00750
0.4	0.55	0.546	0.005	0.005	0.4	0.546	0.275	0.00486
0.4	0.6	0.641	0.005	0.005	0.4	0.641	0.288	0.00371
0.4	0.65	0.714	0.005	0.005	0.4	0.714	0.300	0.00317
0.4	0.7	0.771	0.005	0.005	0.4	0.771	0.311	0.00293
0.4	0.75	0.818	0.005	0.005	0.4	0.818	0.322	0.00284
0.4	0.8	0.856	0.005	0.005	0.4	0.856	0.333	0.00286
0.4	0.85	0.888	0.005	0.005	0.4	0.888	0.343	0.00292
0.4	0.9	0.917	0.005	0.005	0.4	0.917	0.355	0.00301
0.4	0.95	0.945	0.005	0.005	0.4	0.945	0.368	0.00309

**Table SI-8** Fit with the original  $f_{10}$ - $f$ - $X$  data, absolute error in  $X$  constant:

Theoretical sum of squares: 0.000275, Minimum sum of squares: 0.000001  
 95 % confidence limit: 0.000001, 90 % confidence limit: 0.000001  
 (r1,r2)=(0.298,1.998)  
 f1 at t=0: 0.40000

f1	X	XCalc	delta th.	delta calc	delta %
0.450	0.246	0.246	0.005	-0.00010	-0.04
0.500	0.419	0.419	0.005	-0.00046	-0.11
0.550	0.546	0.546	0.005	0.00011	0.02
0.600	0.641	0.641	0.005	0.00021	0.03
0.650	0.714	0.714	0.005	0.00016	0.02
0.700	0.771	0.771	0.005	-0.00036	-0.05
0.750	0.818	0.818	0.005	0.00034	0.04
0.800	0.856	0.856	0.005	0.00017	0.02
0.850	0.888	0.888	0.005	-0.00024	-0.03
0.900	0.917	0.917	0.005	-0.00002	-0.00
0.950	0.945	0.945	0.005	-0.00014	-0.01

av. error 0.034191 %

Error in composition as estimated from fit 0.000269  
 Error in composition from the estimations in measurements 0.005528

The model provides an adequate fit to the data (95 % probability)

**r1 = 0.298 (esd=+-0.001), r2 = 1.998 (esd=+-0.003)**

Screenshot from Contour 2.4.0

**Table SI-9** Data of table SI-5.2 converted to  $f_{10}$ -X-F data where the error in F is obtained through error propagation. Fit with individual error per point used in weighing.

Theoretical sum of squares: 11.000000, Minimum sum of squares: 0.039770  
 95 % confidence limit: 0.077420, 90 % confidence limit: 0.066372  
 (r1,r2)=(0.286,1.974)

f10	X	F1	F1Calc	delta th.	delta calc	delta %
0.400	0.246	0.247	0.247	0.016	-0.00047	-0.19
0.400	0.419	0.261	0.262	0.007	-0.00048	-0.18
0.400	0.546	0.275	0.275	0.005	-0.00010	-0.04
0.400	0.641	0.288	0.288	0.004	0.00003	0.01
0.400	0.714	0.300	0.300	0.003	0.00009	0.03
0.400	0.771	0.311	0.311	0.003	-0.00001	-0.00
0.400	0.818	0.322	0.322	0.003	0.00021	0.06
0.400	0.856	0.333	0.333	0.003	0.00014	0.04
0.400	0.888	0.343	0.343	0.003	-0.00003	-0.01
0.400	0.917	0.355	0.355	0.003	-0.00015	-0.04
0.400	0.945	0.368	0.368	0.003	-0.00047	-0.13
						av. error 0.067053 %

Error in composition as estimated from fit 0.066475  
 Error in composition from the estimations in measurements 1.105542

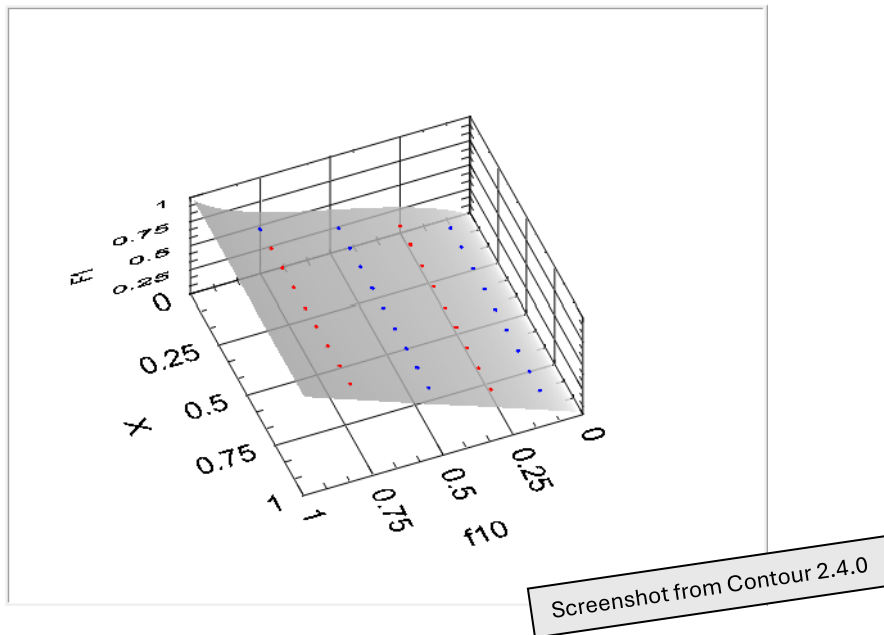
The model provides an adequate fit to the data (95 % probability)

**r1 = 0.286 (esd=+-0.004), r2 = 1.974 (esd=+-0.013)**

Screenshot from Contour 2.4.0

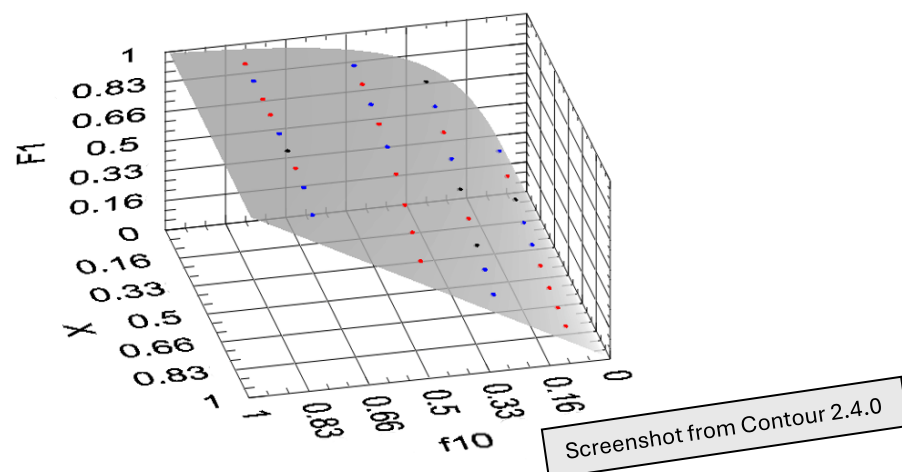


## -6 Effects of systematic errors



**Figure SI-4** For the data in Figure 7 ( $r_1=0.4$ ,  $r_2=0.6$ , modification 1) the residuals space is showing clear systematic trends in the residues.

We now look at the effect of systematic error on a copolymerization with substantial composition drift, given by reactivity ratios  $r_1=13.0$  and  $r_2=0.30$ , where we first added a random error of  $\pm 0.005$  to  $X$  and  $F$ . We first of all look at the residuals, but without systematic errors in  $f_{10}$ .

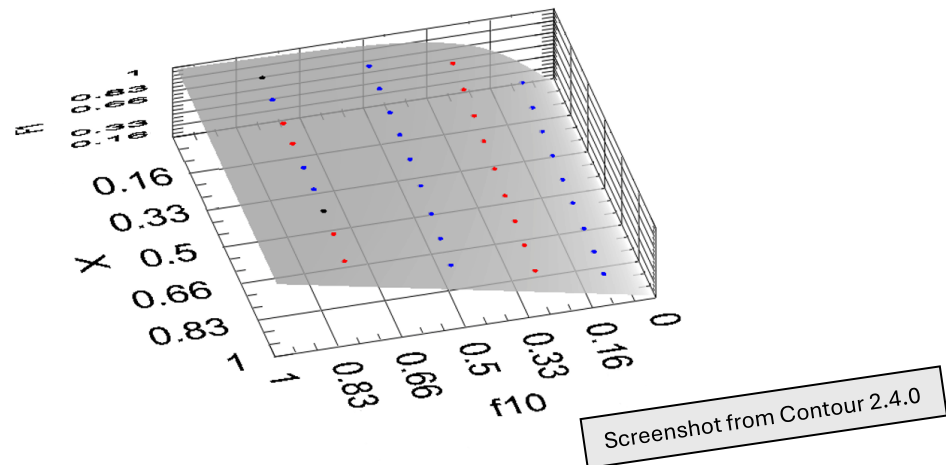


**Figure SI-5** No systematic errors in  $f_{10}$ ,  $r_1=13$ ,  $r_2=0.3$ , residuals space, red is positive, blue negative and black almost zero residues (less than 10% of the estimated errors).



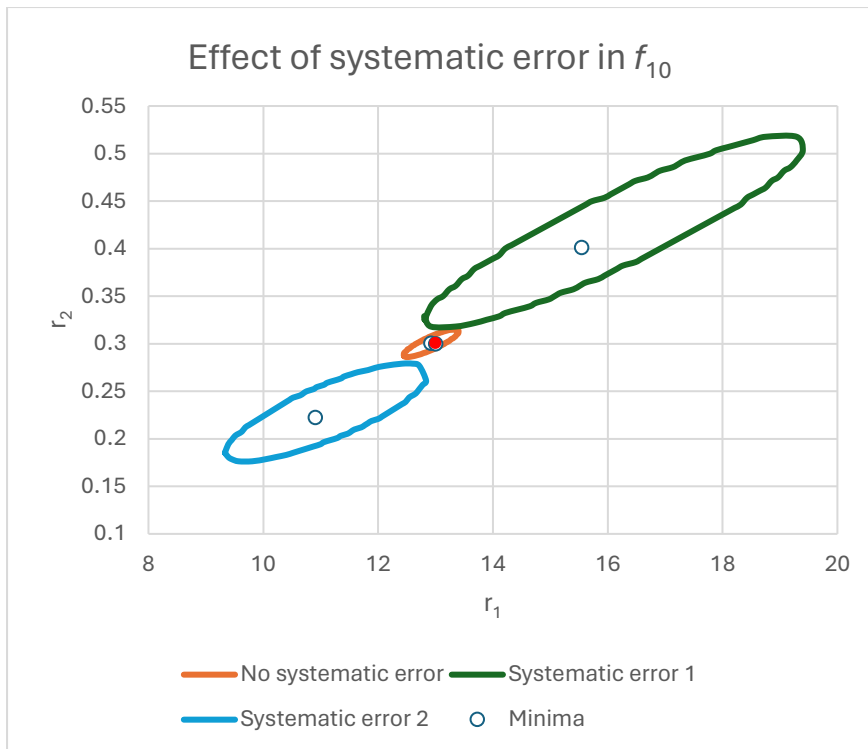
As expected we do not see structure in the residuals, as it should be if no systematic errors are present and the terminal model is adequate.

Now we add a systematic error by alternatingly adding and subtracting 0.01 to  $f_{10}$  (systematic error 1 is + - + -, systematic error 2 is - + - +).



**Figure SI-6** residuals space for a systematic error in  $f_{10}$  (systematic 1)

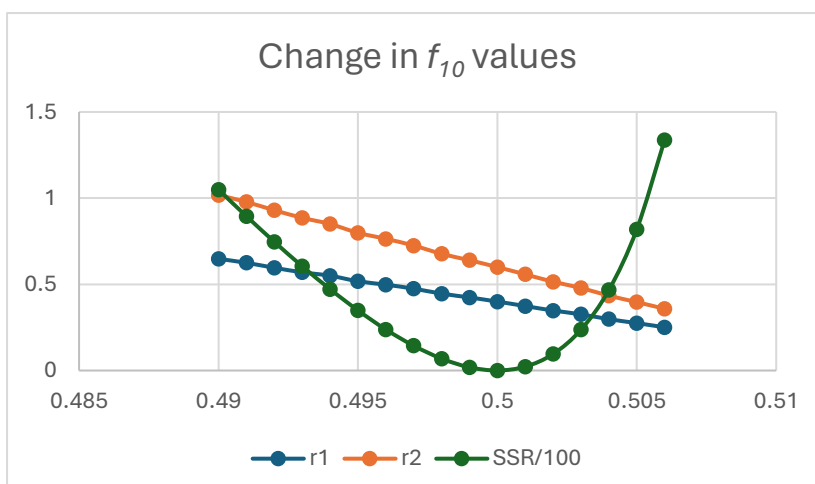
We now see again clear patterns in the residuals.



**Figure SI-7** 95% JCI's obtained through equation 11 for reactivity ratios 13 and 0.3 (red dot), with no systematic errors but with random noise (orange JCI) and with systematic errors 1 (green) and systematic errors 2 (blue).

### 7 Effect of changes in $f_{10}$ value

In a dataset with  $r_1=0.4$  and  $r_2=0.6$  the correct  $f_{10}$  value is 0.5. When only changing the  $f_{10}$  value (introducing a systematic error in the data) the new reactivity ratios are shown below.



**Figure SI-8.** The results are very sensitive for the value of  $f_{10}$ , here shown for simulated  $X$  vs  $f$  data with random noise of  $\pm 0.005$  on  $X$ ,  $r_1=0.4$  (blue),  $r_2=0.6$  (orange) and the true  $f_{10}=0.5$ . Sum of Squares of Residuals (SSR) shown in green.