SI Traceable Isotope Ratios of Carbon Dioxide

– a Feasibility Study

**Lukas Flierl, Anne Stoll-Werian, Olaf Rienitz,
Janine Noordmann, Axel Pramann**

– advancing Optical Isotope Ratio Spectroscopy

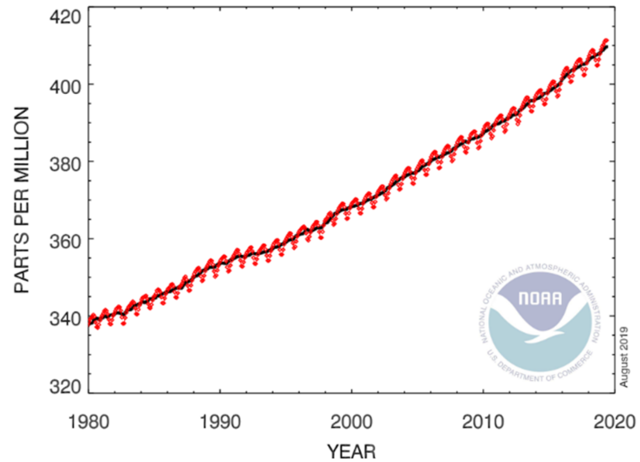
Ivan Prokhorov, Gang Li, Olav Werhahn, Volker Ebert

Physikalisch-Technische Bundesanstalt (PTB)

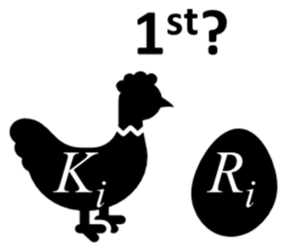
Introduction

- Atmospheric CO_2 concentration heavily increases (> 400 µmol/mol[1])
- Isotope ratios ($R_{^{13}\mathrm{C}/^{12}\mathrm{C}}$ & $R_{^{18}\mathrm{O}/^{16}\mathrm{O}}$) help to discriminate natural from and anthropogenic sources
- International realization of the VPDB scale (NBS-19)
    - Out of stock
    - Not traceable to the SI

→ Gravimetric Mixtures



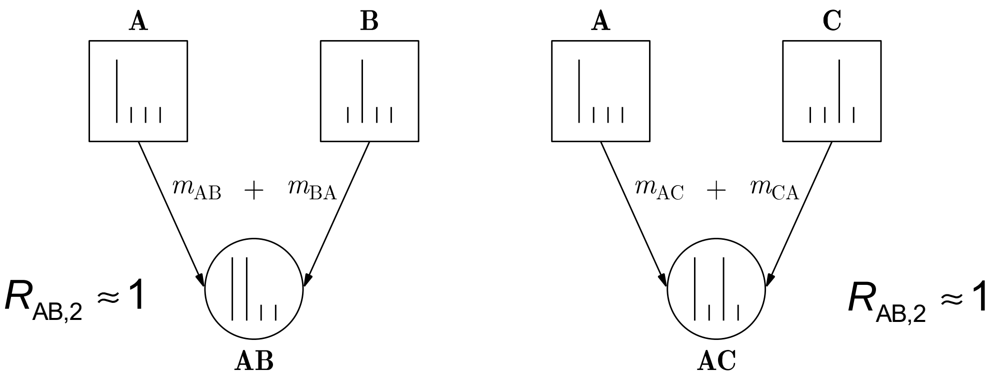
Global atmospheric CO_2 concentration[2].

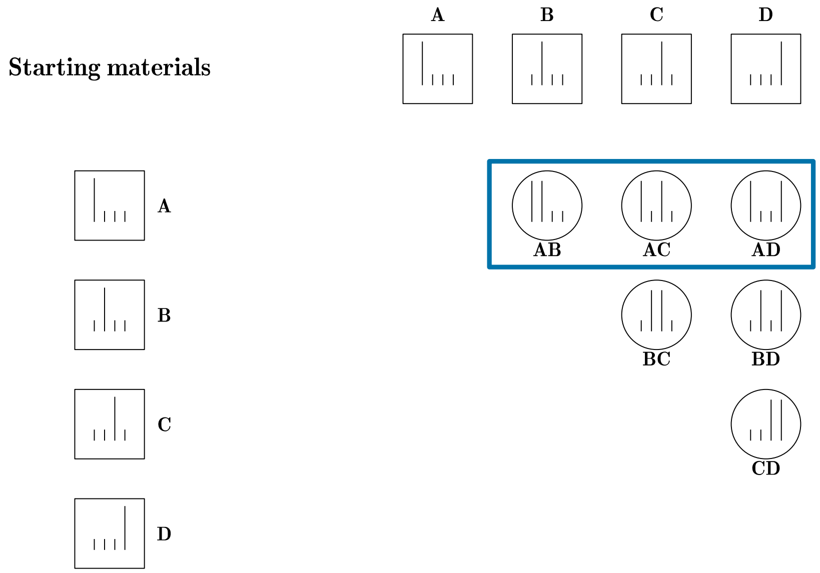


$$R_i = K_i \times R_i^{\mathrm{m}}$$

[1] World Meteorology Organization, Statement on the State of the Global Climate in 2018, WMO, 2019.
[2] National Oceanic and Atmospheric Administration, *Global Monthly Mean CO_2*, Retrieved from https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html, last visited on 14-08-19

Gravimetric Mixtures (I)





$$M_1 \times \left(\frac{1}{m_{AB} \times \left(R^{m}_{A,2} - R^{m}_{AB,2} \right)} - \frac{1}{m_{BA} \times \left(R^{m}_{AB,2} - R^{m}_{B,2} \right)} \right) = K_2 \times M_2 \times \left(\frac{R^{m}_{A,2}}{m_{AB} \times \left(R^{m}_{AB,2} - R^{m}_{A,2} \right)} - \frac{R^{m}_{B,2}}{m_{BA} \times \left(R^{m}_{B,2} - R^{m}_{AB,2} \right)} \right) + K_3 \times M_3 \times \left(\frac{R^{m}_{A,3}}{m_{AB} \times \left(R^{m}_{AB,2} - R^{m}_{A,2} \right)} - \frac{R^{m}_{B,3}}{m_{BA} \times \left(R^{m}_{B,2} - R^{m}_{AB,2} \right)} \right) + K_4 \times M_4 \times \left(\frac{R^{m}_{A,4}}{m_{AB} \times \left(R^{m}_{AB,2} - R^{m}_{A,2} \right)} - \frac{R^{m}_{B,4}}{m_{BA} \times \left(R^{m}_{B,2} - R^{m}_{AB,2} \right)} \right)$$

$$M_1 \times \left(\frac{1}{m_{AC} \times \left(R^{m}_{A,3} - R^{m}_{AC,3} \right)} - \frac{1}{m_{CA} \times \left(R^{m}_{AC,3} - R^{m}_{C,3} \right)} \right) = K_2 \times M_2 \times \left(\frac{R^{m}_{A,2}}{m_{AC} \times \left(R^{m}_{AC,3} - R^{m}_{A,3} \right)} - \frac{R^{m}_{C,2}}{m_{CA} \times \left(R^{m}_{C,3} - R^{m}_{AC,3} \right)} \right) + K_3 \times M_3 \times \left(\frac{R^{m}_{A,3}}{m_{AC} \times \left(R^{m}_{AC,3} - R^{m}_{A,3} \right)} - \frac{R^{m}_{C,3}}{m_{CA} \times \left(R^{m}_{C,3} - R^{m}_{AC,3} \right)} \right) + K_4 \times M_4 \times \left(\frac{R^{m}_{A,4}}{m_{AC} \times \left(R^{m}_{AC,3} - R^{m}_{A,3} \right)} - \frac{R^{m}_{C,4}}{m_{CA} \times \left(R^{m}_{C,3} - R^{m}_{AC,3} \right)} \right)$$

$$M_1 \times \left(\frac{1}{m_{AD} \times \left(R^{m}_{D,4} - R^{m}_{AD,4} \right)} - \frac{1}{m_{DA} \times \left(R^{m}_{AD,4} - R^{m}_{D,4} \right)} \right) = K_2 \times M_2 \times \left(\frac{R^{m}_{A,2}}{m_{AD} \times \left(R^{m}_{AD,4} - R^{m}_{A,4} \right)} - \frac{R^{m}_{D,2}}{m_{DA} \times \left(R^{m}_{D,3} - R^{m}_{AD,3} \right)} \right) + K_3 \times M_3 \times \left(\frac{R^{m}_{A,3}}{m_{AD} \times \left(R^{m}_{AD,4} - R^{m}_{A,4} \right)} - \frac{R^{m}_{D,3}}{m_{DA} \times \left(R^{m}_{D,4} - R^{m}_{AD,4} \right)} \right) + K_4 \times M_4 \times \left(\frac{R^{m}_{A,4}}{m_{AD} \times \left(R^{m}_{AD,4} - R^{m}_{A,4} \right)} - \frac{R^{m}_{D,4}}{m_{DA} \times \left(R^{m}_{D,4} - R^{m}_{AD,4} \right)} \right)$$

Gravimetric Mixtures (II)

$$M_1 \times \left(\frac{1}{m_{\mathrm{AB}} \times \left(R^{\mathrm{m}}_{\mathrm{A},2} - R^{\mathrm{m}}_{\mathrm{AB},2} \right)} - \frac{1}{m_{\mathrm{BA}} \times \left(R^{\mathrm{m}}_{\mathrm{AB},2} - R^{\mathrm{m}}_{\mathrm{B},2} \right)} \right) = K_2 \times M_2 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},2}}{m_{\mathrm{AB}} \times \left(R^{\mathrm{m}}_{\mathrm{AB},2} - R^{\mathrm{m}}_{\mathrm{A},2} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{B},2}}{m_{\mathrm{BA}} \times \left(R^{\mathrm{m}}_{\mathrm{B},2} - R^{\mathrm{m}}_{\mathrm{AB},2} \right)} \right) + K_3 \times M_3 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},3}}{m_{\mathrm{AB}} \times \left(R^{\mathrm{m}}_{\mathrm{AB},2} - R^{\mathrm{m}}_{\mathrm{A},2} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{B},3}}{m_{\mathrm{BA}} \times \left(R^{\mathrm{m}}_{\mathrm{B},2} - R^{\mathrm{m}}_{\mathrm{AB},2} \right)} \right) + K_4 \times M_4 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},4}}{m_{\mathrm{AB}} \times \left(R^{\mathrm{m}}_{\mathrm{AB},2} - R^{\mathrm{m}}_{\mathrm{A},2} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{B},4}}{m_{\mathrm{BA}} \times \left(R^{\mathrm{m}}_{\mathrm{B},2} - R^{\mathrm{m}}_{\mathrm{AB},2} \right)} \right)$$

$$M_1 \times \left(\frac{1}{m_{\mathrm{AC}} \times \left(R^{\mathrm{m}}_{\mathrm{A},3} - R^{\mathrm{m}}_{\mathrm{AC},3} \right)} - \frac{1}{m_{\mathrm{CA}} \times \left(R^{\mathrm{m}}_{\mathrm{AC},3} - R^{\mathrm{m}}_{\mathrm{C},3} \right)} \right) = K_2 \times M_2 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},2}}{m_{\mathrm{AC}} \times \left(R^{\mathrm{m}}_{\mathrm{AC},3} - R^{\mathrm{m}}_{\mathrm{A},3} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{C},2}}{m_{\mathrm{CA}} \times \left(R^{\mathrm{m}}_{\mathrm{C},3} - R^{\mathrm{m}}_{\mathrm{AC},3} \right)} \right) + K_3 \times M_3 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},3}}{m_{\mathrm{AC}} \times \left(R^{\mathrm{m}}_{\mathrm{AC},3} - R^{\mathrm{m}}_{\mathrm{A},3} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{C},3}}{m_{\mathrm{CA}} \times \left(R^{\mathrm{m}}_{\mathrm{C},3} - R^{\mathrm{m}}_{\mathrm{AC},3} \right)} \right) + K_4 \times M_4 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},4}}{m_{\mathrm{AC}} \times \left(R^{\mathrm{m}}_{\mathrm{AC},3} - R^{\mathrm{m}}_{\mathrm{A},3} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{C},4}}{m_{\mathrm{CA}} \times \left(R^{\mathrm{m}}_{\mathrm{C},3} - R^{\mathrm{m}}_{\mathrm{AC},3} \right)} \right)$$

$$M_1 \times \left(\frac{1}{m_{\mathrm{AD}} \times \left(R^{\mathrm{m}}_{\mathrm{D},4} - R^{\mathrm{m}}_{\mathrm{AD},4} \right)} - \frac{1}{m_{\mathrm{DA}} \times \left(R^{\mathrm{m}}_{\mathrm{AD},4} - R^{\mathrm{m}}_{\mathrm{D},4} \right)} \right) = K_2 \times M_2 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},2}}{m_{\mathrm{AD}} \times \left(R^{\mathrm{m}}_{\mathrm{AD},4} - R^{\mathrm{m}}_{\mathrm{A},4} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{D},2}}{m_{\mathrm{DA}} \times \left(R^{\mathrm{m}}_{\mathrm{D},3} - R^{\mathrm{m}}_{\mathrm{AD},3} \right)} \right) + K_3 \times M_3 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},3}}{m_{\mathrm{AD}} \times \left(R^{\mathrm{m}}_{\mathrm{AD},4} - R^{\mathrm{m}}_{\mathrm{A},4} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{D},3}}{m_{\mathrm{DA}} \times \left(R^{\mathrm{m}}_{\mathrm{D},4} - R^{\mathrm{m}}_{\mathrm{AD},4} \right)} \right) + K_4 \times M_4 \times \left(\frac{R^{\mathrm{m}}_{\mathrm{A},4}}{m_{\mathrm{AD}} \times \left(R^{\mathrm{m}}_{\mathrm{AD},4} - R^{\mathrm{m}}_{\mathrm{A},4} \right)} - \frac{R^{\mathrm{m}}_{\mathrm{D},4}}{m_{\mathrm{DA}} \times \left(R^{\mathrm{m}}_{\mathrm{D},4} - R^{\mathrm{m}}_{\mathrm{AD},4} \right)} \right)$$

system of linear equations
solvable for K_2, K_3 & K_4

$$\rightarrow K_y = f\left(M_1, \ldots, M_4, m_{\mathrm{AB}}, \ldots, m_{\mathrm{DA}}, R^{\mathrm{m}}_{2,\mathrm{A}}, \ldots, R^{\mathrm{m}}_{4,\mathrm{AD}}\right)$$

Solving a Linear System

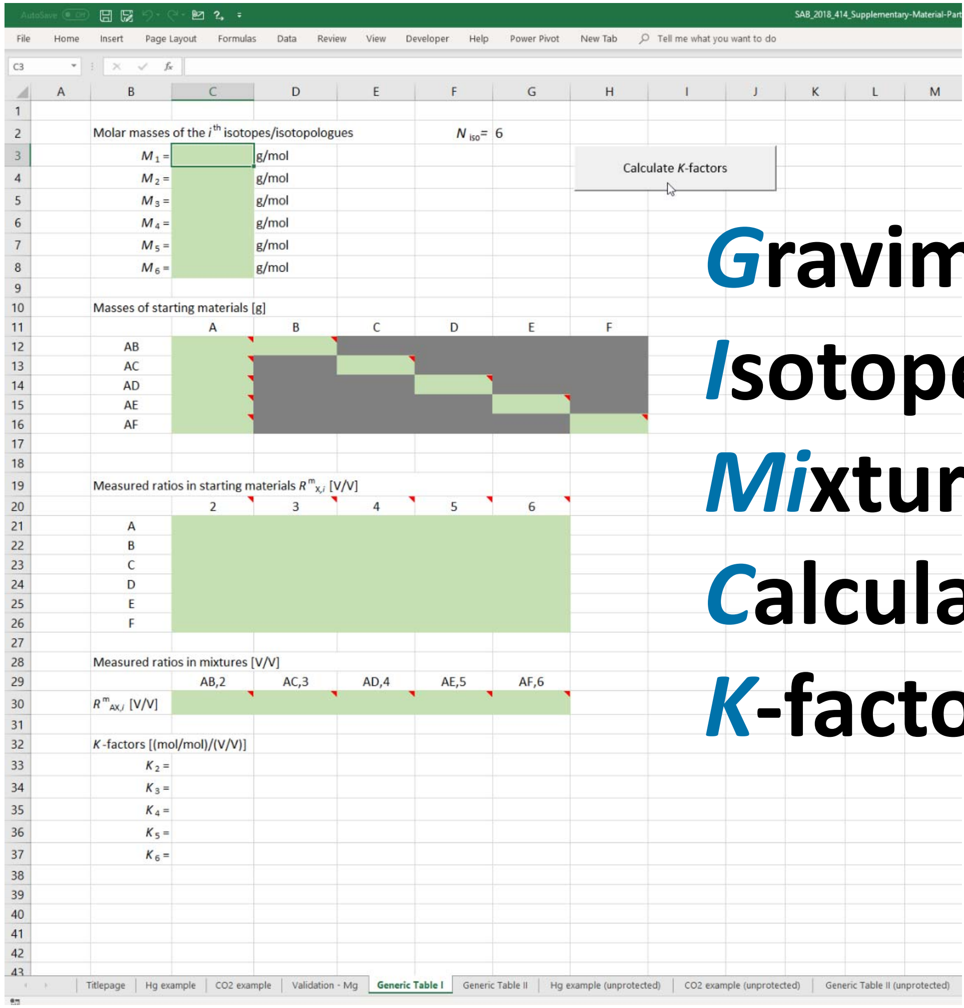
$$K_2 - 2\times K_3 + K_4 = 2$$

$$K_2 + 5\times K_3 + 2\times K_4 = 3$$

$$K_2 - 3\times K_3 + K_4 = 1$$

- Cramer‘s rule
- QR factorization
- Cholesky decomposition
- Gaussian Elimination
- …

Generic Solving Routine (I) - *GIMiCK*



Gravimetric
Isotope
Mixtures
Calculator for
***K*-factors**

- Up to $N_{iso} = 12$
- Dynamic input mask
- Sets up system of linear equations
- Gaussian elimination (non-iterative!)

A. Stoll-Werian, L. Flierl, O. Rienitz, J. Noordmann, R. Kessel, A. Pramann, Spectrochim. Acta B 2019

Generic Solving Routine (II)

Generic expression

$$\sum_{i=2}^{N_{\text{iso}}}\left[K_i \times M_i \times \left(\frac{R^{\text{m}}_{\text{A},i}}{m_{\text{AY}} \times \left(R^{\text{m}}_{\text{AY},j} - R^{\text{m}}_{\text{A},j}\right)} - \frac{R^{\text{m}}_{\text{Y},i}}{m_{\text{YA}} \times \left(R^{\text{m}}_{\text{Y},j} - R^{\text{m}}_{\text{AY},j}\right)}\right)\right] = M_1 \times \left(\frac{1}{m_{\text{AY}} \times \left(R^{\text{m}}_{\text{AY},j} - R^{\text{m}}_{\text{A},j}\right)} - \frac{1}{m_{\text{YA}} \times \left(R^{\text{m}}_{\text{Y},j} - R^{\text{m}}_{\text{AY},j}\right)}\right)$$

α-terms γ-terms

alter i

alter Y

$$\left(\begin{array}{cccc|c} \alpha_1 \times K_2 & \alpha_2 \times K_3 & \cdots & \alpha_{N_{\text{iso}}-1} \times K_{N_{\text{iso}}} & \gamma_1 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \alpha_{(N_{\text{iso}}-1)^2-(N_{\text{iso}}-2)} \times K_2 & \alpha_{(N_{\text{iso}}-1)^2-(N_{\text{iso}}-3)} \times K_3 & \cdots & \alpha_{(N_{\text{iso}}-1)^2} \times K_{N_{\text{iso}}} & \gamma_{N_{\text{iso}}-1} \end{array}\right) = X$$

$i \in \{2, 3, \ldots, N_{\text{iso}}\}$

$Y \in \{\text{B}, \text{C}, \ldots, \text{XY}\}$

Generic Solving Routine (III)

$$\left(\begin{array}{cccc|c} \alpha_1 \times K_2 & \alpha_2 \times K_3 & \cdots & \alpha_{N_{\mathrm{iso}}-1} \times K_{N_{\mathrm{iso}}} & \gamma_1 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \alpha_{(N_{\mathrm{iso}}-1)^2-(N_{\mathrm{iso}}-2)} \times K_2 & \alpha_{(N_{\mathrm{iso}}-1)^2-(N_{\mathrm{iso}}-3)} \times K_3 & \cdots & \alpha_{(N_{\mathrm{iso}}-1)^2} \times K_{N_{\mathrm{iso}}} & \gamma_{N_{\mathrm{iso}}-1} \end{array}\right) = X$$

several computational steps

$$\left(\begin{array}{cccc|c} \alpha_1 \times K_2 & \alpha_2 \times K_3 & \cdots & \alpha_{N_{\mathrm{iso}}-1} \times K_{N_{\mathrm{iso}}} & \gamma_1 \\ 0 & \beta_2 \times K_3 & \cdots & \alpha_{N_{\mathrm{iso}}-1} \times K_{N_{\mathrm{iso}}} & \delta_2 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & \beta_{(N_{\mathrm{iso}}-1)^2} \times K_{N_{\mathrm{iso}}} & \delta_{N_{\mathrm{iso}}-1} \end{array}\right)$$

backward substitution

Advantages of Direct Methods

- Not effected by possible convergence issues or local minima
- Uncertainty propagation (GUM) is much more straightforward
  - Propagation of variances
  - Monte Carlo simulation

$$K_2 = \frac{M_1 \times N_2}{M_2 \times D}$$

$$\begin{aligned}
N_2 = & -m_{AB} \times m_{AC} \times m_{AD} \times (R^{m}_{A,2} - R^{m}_{AB,2}) \times (R^{m}_{A,3} - R^{m}_{AC,3}) \times (R^{m}_{A,4} - R^{m}_{AC,4}) \times (R^{m}_{B,3}(R^{m}_{D,4} - R^{m}_{C,4}) + R^{m}_{B,4} \times (R^{m}_{C,3} - R^{m}_{D,3}) - R^{m}_{C,3} \times R^{m}_{D,4} + R^{m}_{C,4} \times R^{m}_{D,3}) \\
& -m_{AB} \times m_{AC} \times m_{DA} \times (R^{m}_{A,2} - R^{m}_{AB,2}) \times (R^{m}_{A,3} - R^{m}_{AC,3}) \times (R^{m}_{AC,4} - R^{m}_{D,4}) \times (R^{m}_{A,3} \times (R^{m}_{B,4} - R^{m}_{C,4}) + R^{m}_{A,4} \times (R^{m}_{C,3} - R^{m}_{B,3}) + R^{m}_{B,3} \times R^{m}_{C,4} - R^{m}_{B,4} \times R^{m}_{C,3}) \\
& -m_{AB} \times m_{AD} \times m_{CA} \times (R^{m}_{A,2} - R^{m}_{AB,2}) \times (R^{m}_{A,4} - R^{m}_{AC,4}) \times (R^{m}_{AC,3} - R^{m}_{C,3}) \times (R^{m}_{A,3} \times (R^{m}_{D,4} - R^{m}_{B,4}) + R^{m}_{A,4} \times (R^{m}_{B,3} - R^{m}_{D,3}) - R^{m}_{B,3} \times R^{m}_{D,4} + R^{m}_{B,4} \times R^{m}_{D,3}) \\
& -m_{AC} \times m_{AD} \times m_{BA} \times (R^{m}_{A,3} - R^{m}_{AC,3}) \times (R^{m}_{A,4} - R^{m}_{AC,4}) \times (R^{m}_{AB,2} - R^{m}_{B,2})(R^{m}_{A,3} \times (R^{m}_{C,4} - R^{m}_{D,4}) + R^{m}_{A,4} \times (R^{m}_{D,3} - R^{m}_{C,3}) + R^{m}_{C,3} \times R^{m}_{D,4} - R^{m}_{C,4} \times R^{m}_{D,3})
\end{aligned}$$

$$\begin{aligned}
D = & \, m_{AB} \times m_{AC} \times m_{AD} \times (R^{m}_{A,2} - R^{m}_{AB,2}) \times (R^{m}_{A,3} - R^{m}_{AC,3}) \times (R^{m}_{A,4} - R^{m}_{AD,4}) \times (-R^{m}_{B,2} \times R^{m}_{C,3} \times R^{m}_{D,4} + R^{m}_{B,2} \times R^{m}_{C,4} \times R^{m}_{D,3} + R^{m}_{B,3} \times R^{m}_{C,2} \times R^{m}_{D,4} - R^{m}_{B,3} \times R^{m}_{C,4} \times R^{m}_{D,2} - R^{m}_{B,4} \times R^{m}_{C,2} \times R^{m}_{D,3} + R^{m}_{B,4} \times R^{m}_{C,3} \times R^{m}_{D,2}) \\
& -m_{AB} \times m_{AC} \times m_{DA} \times (R^{m}_{A,2} - R^{m}_{AB,2}) \times (R^{m}_{A,3} - R^{m}_{AC,3}) \times (R^{m}_{AD,4} - R^{m}_{D,4}) \times (-R^{m}_{A,2} \times R^{m}_{B,3} \times R^{m}_{C,4} + R^{m}_{A,2} \times R^{m}_{B,4} \times R^{m}_{C,3} + R^{m}_{A,3} \times R^{m}_{B,2} \times R^{m}_{C,4} - R^{m}_{A,3} \times R^{m}_{B,4} \times R^{m}_{C,2} - R^{m}_{A,4} \times R^{m}_{B,2} \times R^{m}_{C,3} + R^{m}_{A,4} \times R^{m}_{B,3} \times R^{m}_{C,2}) \\
& +m_{AB} \times m_{AD} \times m_{CA} \times (R^{m}_{A,2} - R^{m}_{AB,2}) \times (R^{m}_{A,4} - R^{m}_{AD,4}) \times (R^{m}_{AC,3} - R^{m}_{C,3}) \times (-R^{m}_{A,2} \times R^{m}_{B,3} \times R^{m}_{D,4} + R^{m}_{A,2} \times R^{m}_{B,4} \times R^{m}_{D,3} + R^{m}_{A,3} \times R^{m}_{B,2} \times R^{m}_{D,4} - R^{m}_{A,3} \times R^{m}_{B,4} \times R^{m}_{D,2} - R^{m}_{A,4} \times R^{m}_{B,2} \times R^{m}_{D,3} + R^{m}_{A,4} \times R^{m}_{B,3} \times R^{m}_{D,2}) \\
& +m_{AC} \times m_{AD} \times m_{BA} \times (R^{m}_{A,3} - R^{m}_{AC,3}) \times (R^{m}_{A,4} - R^{m}_{AD,4}) \times (R^{m}_{AB,2} - R^{m}_{B,2}) \times (R^{m}_{A,2} \times R^{m}_{C,3} \times R^{m}_{D,4} - R^{m}_{A,2} \times R^{m}_{C,4} \times R^{m}_{D,3} - R^{m}_{A,3} \times R^{m}_{C,2} \times R^{m}_{D,4} + R^{m}_{A,3} \times R^{m}_{C,4} \times R^{m}_{D,2} + R^{m}_{A,4} \times R^{m}_{C,2} \times R^{m}_{D,3} - R^{m}_{A,4} \times R^{m}_{C,3} \times R^{m}_{D,2})
\end{aligned}$$

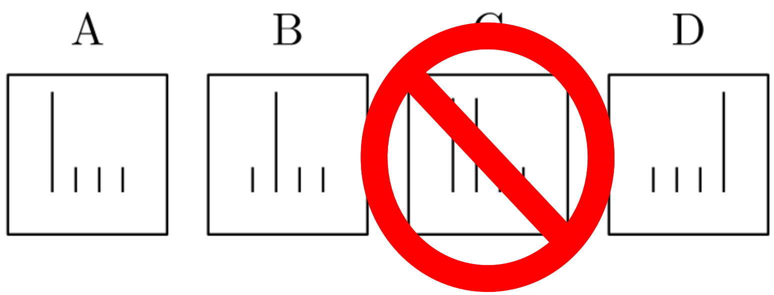
Condition for Solvability

$$\det(\mathbf{A}) = \begin{vmatrix} \alpha_1 & \alpha_2 & \alpha_{N_{\text{iso}}-1} \\ \vdots & \vdots & \vdots \\ \alpha_{(N_{\text{iso}}-1)^2-(N_{\text{iso}}-2)} & \alpha_{(N_{\text{iso}}-1)^2-(N_{\text{iso}}-3)} & \alpha_{(N_{\text{iso}}-1)^2} \end{vmatrix} \neq 0$$

$$\alpha_y = K_i \times M_i \times \left(\frac{R^{\text{m}}_{\text{A},i}}{m_{\text{AY}} \times \left(R^{\text{m}}_{\text{AY},j} - R^{\text{m}}_{\text{A},j} \right)} - \frac{R^{\text{m}}_{\text{Y},i}}{m_{\text{YA}} \times \left(R^{\text{m}}_{\text{Y},j} - R^{\text{m}}_{\text{AY},j} \right)} \right)$$

If det(**A**) = 0

⟶ No solution or countless



Preparation of Blends (I)

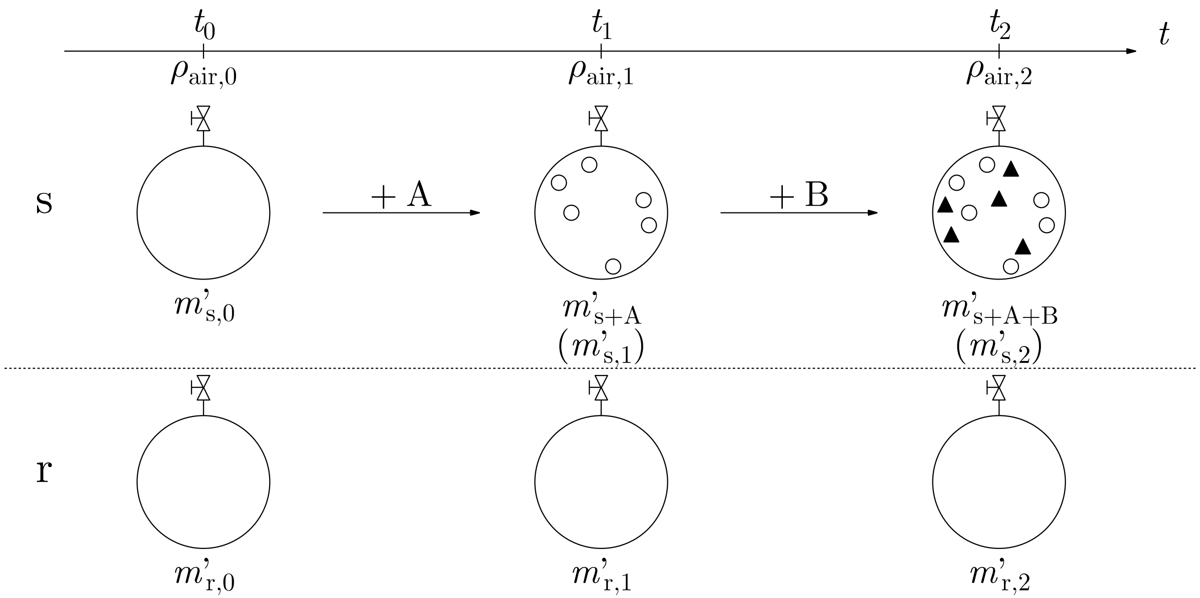
- High-vacuum line

  ($p \approx 1\times10^{-5}$ Pa)
- Set up from CF flanges
- Custom-made gas vessels
- Made from electropolished stainless steel

  ($V \approx 800$ mL, $m_{tare} \approx 730$ g)

Preparation of Blends (II)

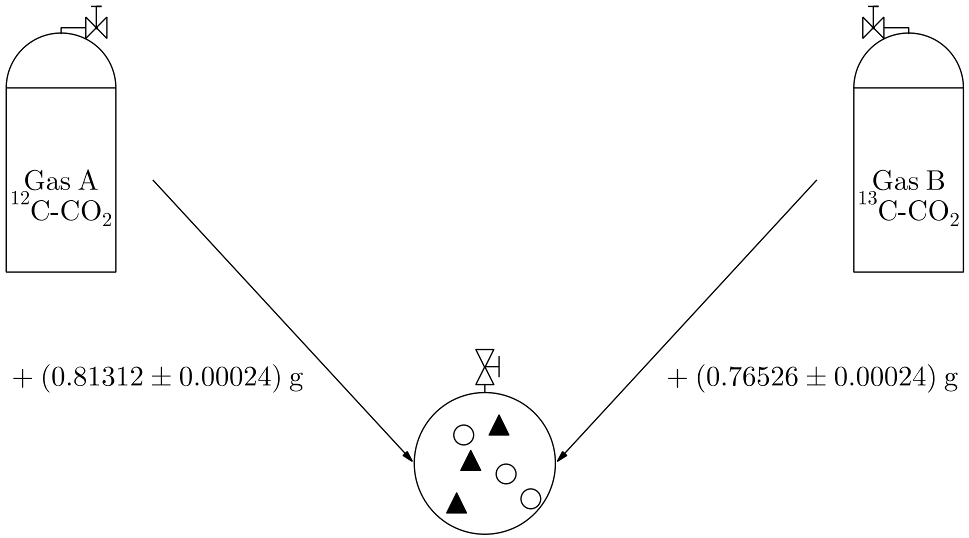
1. Heating and evacuating of gas containers (≈ 200°C, 24 h)
2. Weighing against evacuated reference container
3. Cryogenically trapping amount of gas A (m_A)
4. Weighing against evacuated reference container
5. Cryogenically trapping amount of gas B (m_B)
6. Weighing against evacuated reference container
7. Calculating buoyancy corrected values of m_A and m_B
8. Long-time measurement (≈ 4.5 h) of the blend and both parent materials using IRMS

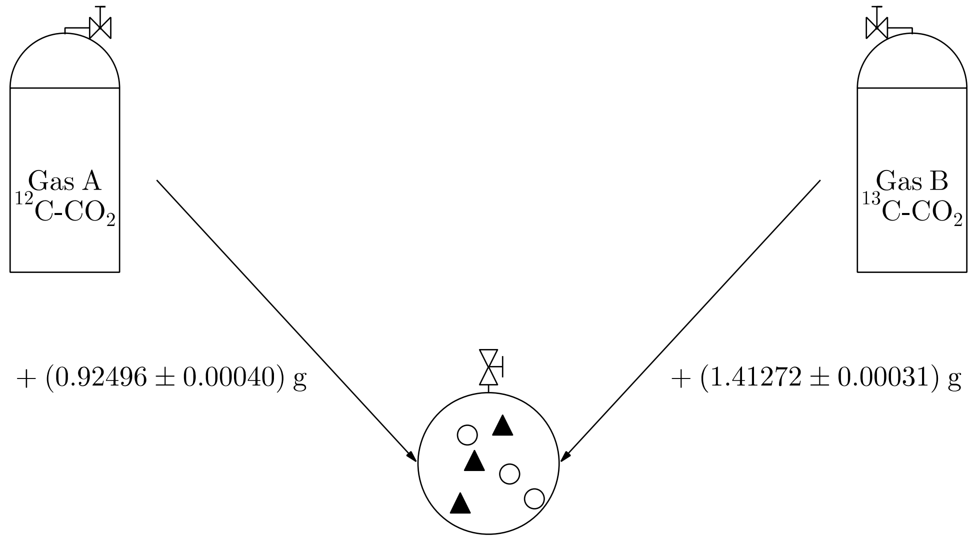


L. Flierl, O. Rienitz, A. Pramann, Anal. Bioanal. Chem., accepted, 2020.

First Blends

1^{st} & 2^{nd} blend mixed from
gas A ($x(^{12}C) \approx 0.9998(1)$ mol/mol) + gas B ($x(^{13}C) \approx 0.993(1)$ mol/mol)

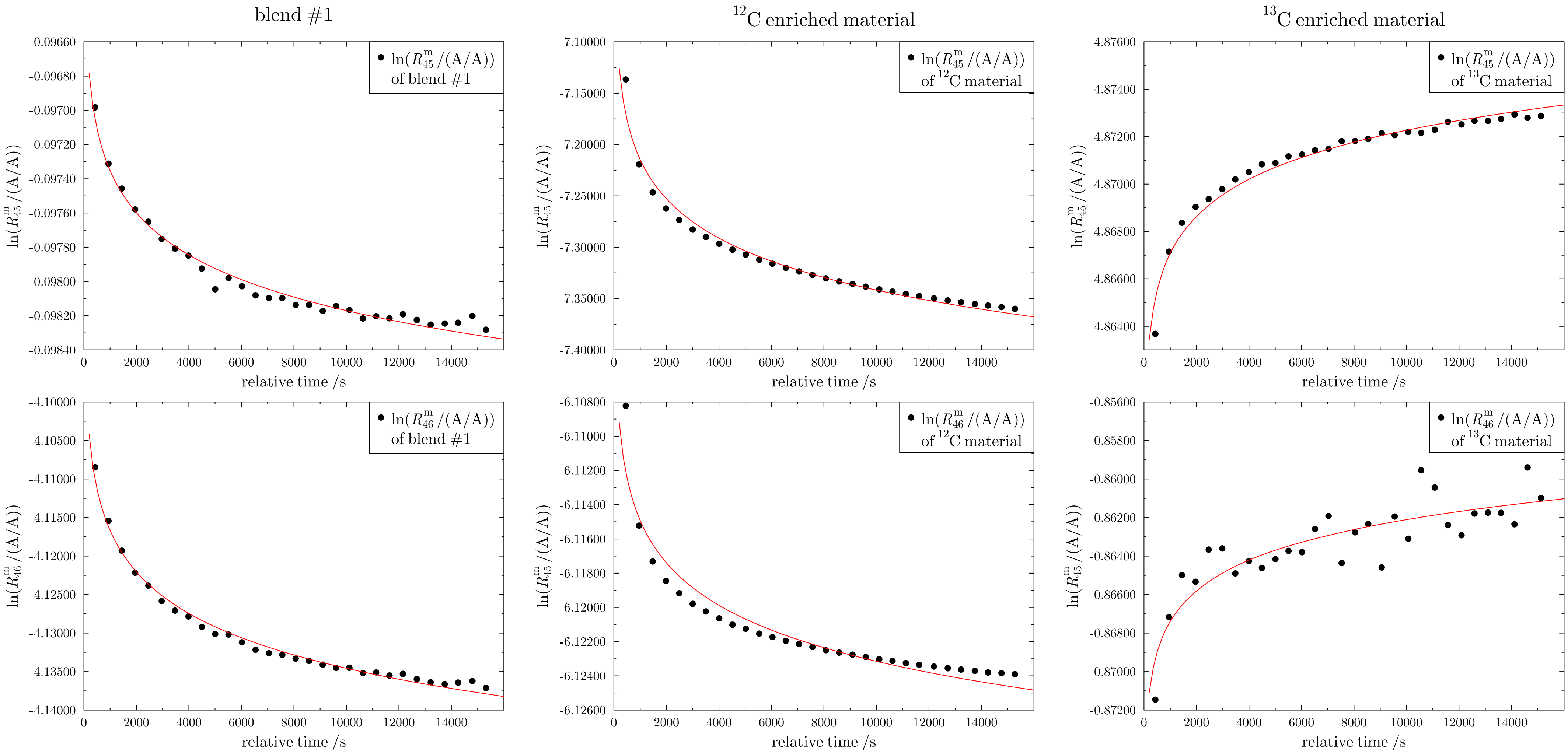




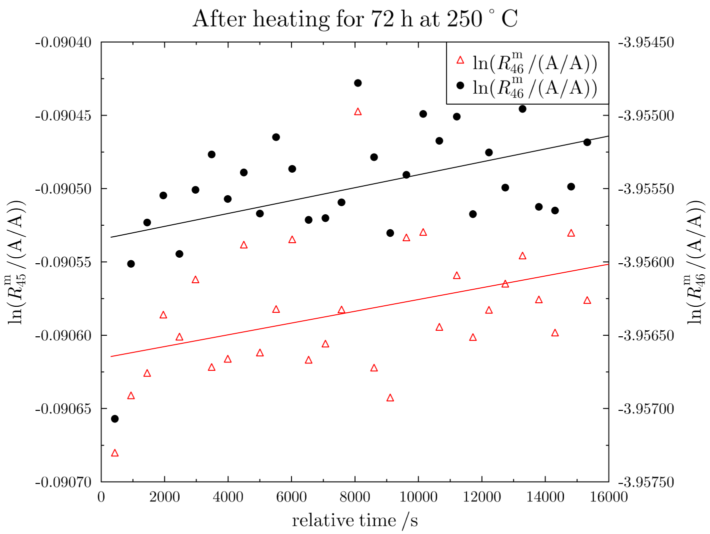
$R_{45}^{\text{theo}} = (0.8791 \pm 0.0040)$ mol/mol
$R_{46}^{\text{theo}} = (0.0072 \pm 0.0021)$ mol/mol

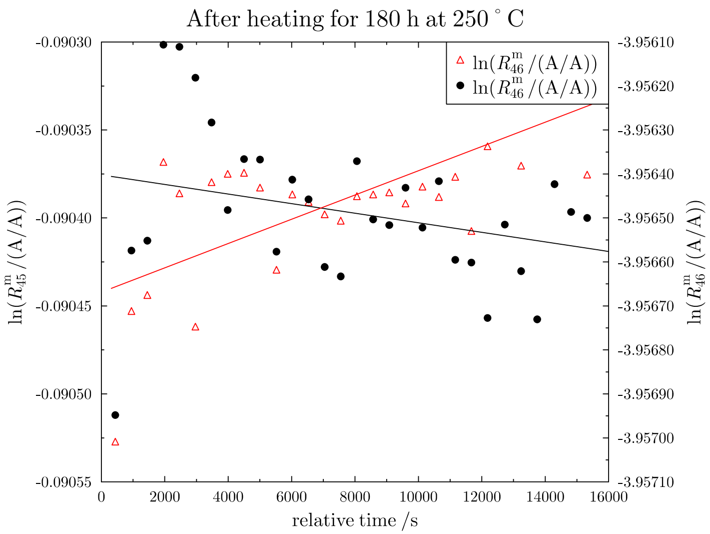
$R_{45}^{\text{theo}} = (1.4207 \pm 0.0067)$ mol/mol
$R_{46}^{\text{theo}} = (0.0093 \pm 0.0033)$ mol/mol

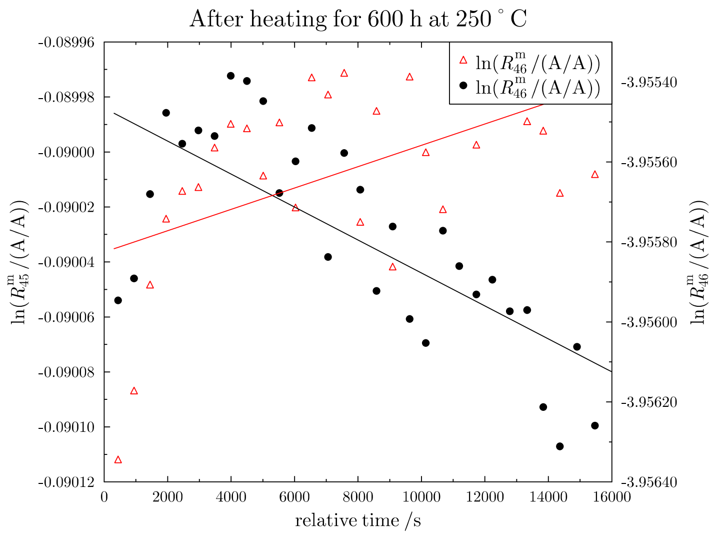
First Measurements of Blend #1



Isotope Equilibrium of Carbon Dioxide (I)



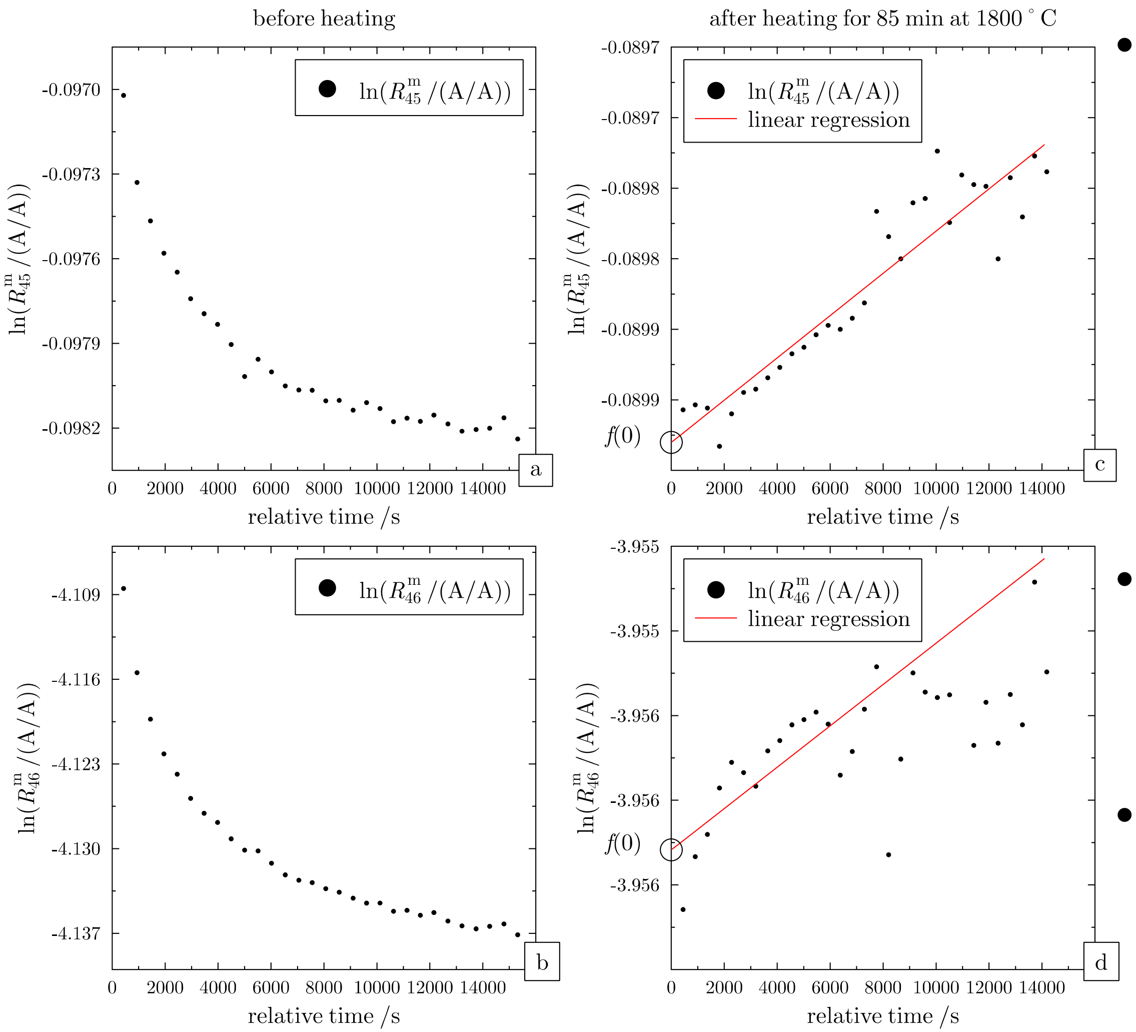




$$^{16}O\,^{12}C\,^{16}O + {}^{18}O\,^{12}C\,^{18}O \rightleftharpoons 2\,^{16}O\,^{12}C\,^{18}O$$

$$^{16}O\,^{12}C\,^{16}O + {}^{18}O\,^{13}C\,^{18}O \rightleftharpoons {}^{16}O\,^{12}C\,^{18}O + {}^{16}O\,^{13}C\,^{18}O$$

Isotope Equilibrium of Carbon Dioxide (III)



- Linear regression & extrapolation to t = 0

$$R^{m}_{45,0} = (0.913995 \pm 0.000016)\ \text{A/A}$$

$$R^{m}_{46,0} = (0.0191411 \pm 0.0000034)\ \text{A/A}$$

$$R^{theo}_{45} = (0.8791 \pm 0.0040)\ \text{mol/mol}$$

$$R^{theo}_{46} = (0.0072 \pm 0.0021)\ \text{mol/mol}$$

- Calculating R_{13}, R_{17} and R_{18}[1]

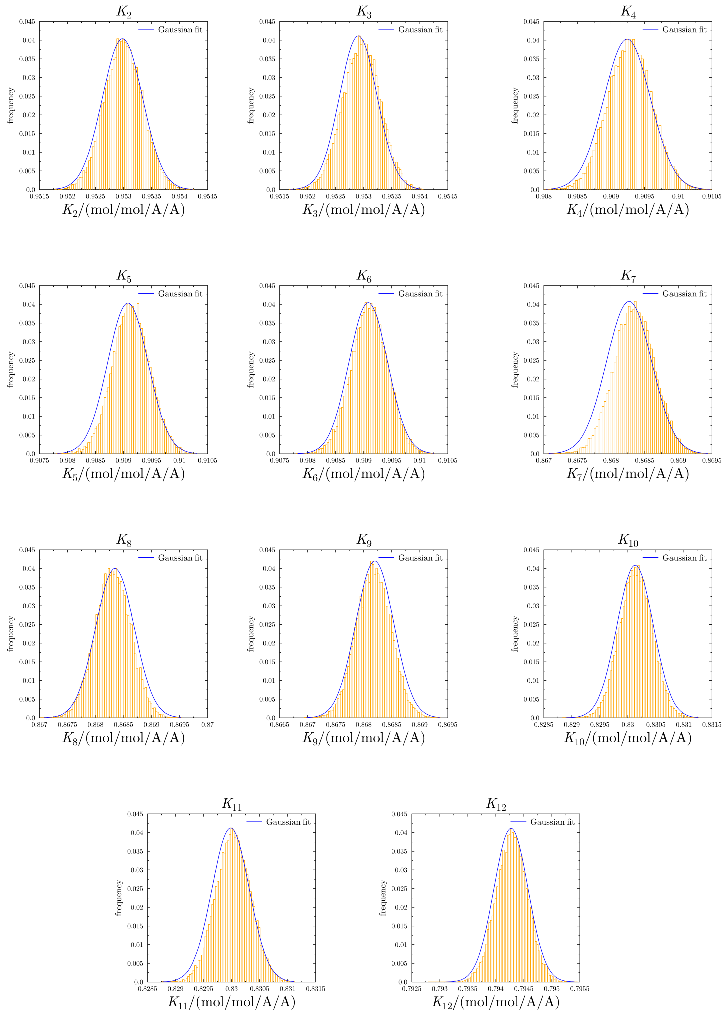
$$R_{46} = -3 \times K^2 \times R_{18}^{2\times\lambda} + 2 \times K \times R_{45} \times R_{18}^{\lambda} + 2 \times R_{18}$$

- Calculating all istopologue ratios and uncertainties

Monte Carlo Simulation

[1] J. Santrock, S. Studley, and J. Hayes, Anal. Chem., 57, 1985.

Monte Carlo Simulation of all 11 *K*-factors



- Used made-up data set (R^{m} , M , m) (from *GIMiCK*[1])
- Added uncertainties from isotopologue ratio derivation and mixing (e.g. $u(m_A)$)
- Monte Carlo Simulation with 20 000 runs

R_{13} = (0.0111980 ± 0.0000091) mol/mol (0.081 %), (k =2)

R_{17} = (0.00037990 ± 0.000000030) mol/mol (0.080 %), (k =2)

R_{18} = (0.0020052 ± 0.0000016) mol/mol (0.081 %), (k =2)

[2] L. Flierl, O. Rienitz, R. Kessel, A. Pramann, Spectrochim. Acta B, in preparation

[1] A. Stoll-Werian, L. Flierl, O. Rienitz, J. Noordmann, R. Kessel, A. Pramann, Spectrochim. Acta B 2019

Summary & Outlook

- Concept of gravimetric mixtures
- Non-iterative calculation of *K*-factors for $N_{iso} \geq 4$ → Adapt math for isotope equilibrium
- EXCEL® based tool available → Monte Carlo Module
- First binary mixtures of enriched/depleted CO_2 → Further blends for studying reproducibility & ^{18}O enriched/depleted materials