Physikalisch-Technische Bundesanstalt
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Isotope Analysis as a tool for climate metrology at PTB: a novel approach to oxygen-17 correction

Introduction

- isotope deltas ($\delta^{13}C$ & $\delta^{18}O_{VPDB\text{-}CO_2}$) serve as useful proxies
- correct data evaluation, including ^{17}O correction, is crucial
- numeric methods are necessary due to measurement limitations

$$0 = R_{46} + 3K^2 R_{18}^{2\lambda} - 2R_{45} K R_{18}^{\lambda} - 2R_{18} \quad (1)$$

- Brand et al. [1] introduced linear approximations for easy handling, unified parameters (λ, $R_{13,VPDB}$, $R_{18,VPDB\text{-}CO_2}$), isotope delta formulation, and simplified uncertainty assessment

$$\delta^{13}C_{VPDB} \approx \delta_{45} + \frac{2 \cdot R_{17,VPDB\text{-}CO_2} \left(\delta_{45} - \lambda \cdot \delta_{46}\right)}{R_{13,VPDB}} \quad (2a)$$

$$\delta^{18}O_{VPDB\text{-}CO_2} \approx \frac{\delta_{46} - 0.0021 \cdot \delta^{13}C_{VPDB}}{0.99904} \quad (2b)$$

Motivation

- enhance accuracy
- evaluate uncertainty using the GUM [2]
- streamline usability with an Excel Add-in

Alternative Algorithm

- Approximating equation (1) with a second-degree Taylor polynomial yields:

$$\delta^{13}C = \frac{\left(\delta_{45}+1\right) R_{45,VPDB\text{-}CO_2} - 2K\left(\left(\delta_{18}+1\right) R_{18,VPDB\text{-}CO_2}\right)^{\lambda}}{R_{13,VPDB\text{-}CO_2}} - 1 \quad (3a)$$

$$\delta^{18}O \approx \frac{3R_{17,VPDB\text{-}CO_2}^2 - 2\left(\delta_{45}+1\right) R_{45,VPDB\text{-}CO_2} R_{17,VPDB\text{-}CO_2} - 2R_{18,VPDB\text{-}CO_2} + \left(\delta_{46}+1\right) R_{46,VPDB\text{-}CO_2}}{2\left(-3\lambda R_{17,VPDB\text{-}CO_2}^2 + \lambda\left(\delta_{45}+1\right) R_{45,VPDB\text{-}CO_2} R_{17,VPDB\text{-}CO_2}^2 + R_{18,VPDB\text{-}CO_2}\right)} \quad (3b)$$

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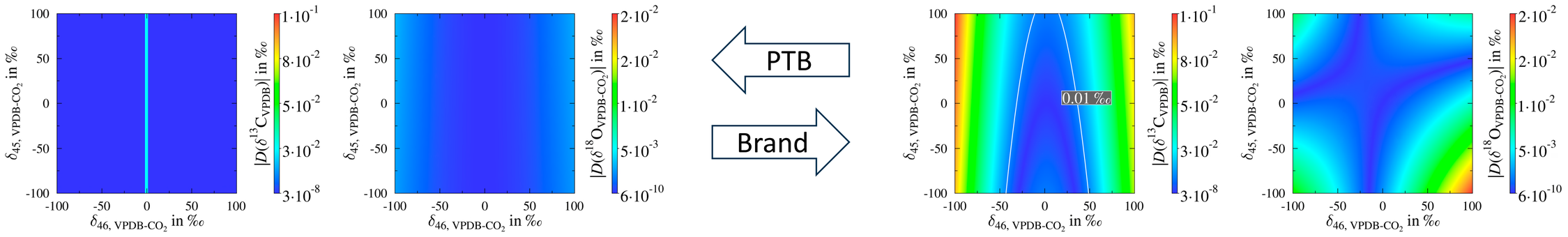
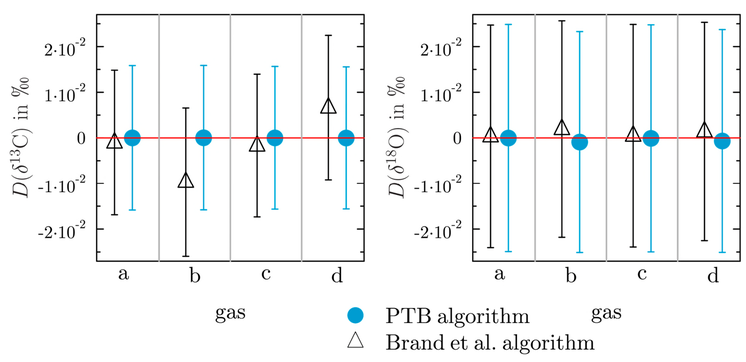
Simulation



Real examples (PTB results from CCQM-P204 [3])



Improvements

- high accuracy across a wider range ($|D| \ll 0.01$ ‰)
- uncertainty evaluation compliant with GUM standards
- handy Excel Add-in with normalization, customizable parameters, and multiple algorithms

Innovation Cluster for Environment and Climate (IC-U)

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[1] W. A. Brand, S. S. Assonov, and T. B. Coplen, "Correction for the 17O interference in δ(^{13}C) measurements when analyzing CO_2 with stable isotope mass spectrometry (IUPAC Technical Report)," Pure Appl. Chem., vol. 82, no. 8, pp. 1719–1733, Jan. 2010, doi: 10.1351/pac-rep-09-01-05.
[2] BIPM et al., "Evaluation of measurement data — An introduction to the "Guide to the expression of uncertainty in measurement" and related documents.". Available: https://www.bipm.org/documents/20126/2071204/JCGM_104_2009.pdf/19e0a96c-6cf3-a056-4634-4465c576e513
[3] J. Viallon et al., "Final report of CCQM-P204, comparison on CO2 isotope ratios in pure CO2," Metrologia, vol. 60, no. 1A, p. 8026, Nov. 2023, doi: 10.1088/0026-1394/60/1A/08026.