

Fragment ion measurement of $^{17}\text{O}^+$ and $^{13}\text{C}^+$ of CO_2 with MAT253-Ultra

GETACHEW ADNEW^{1*}, MAGDALENA HOFMAAN¹, AMZAD LASKAR¹, DIPAYAN PAUL², ELENA POPA¹, WOUTER PETERS^{2,3}, THOMAS RÖCHMANN¹

¹Institute for Marine and Atmospheric Research Utrecht, Utrecht University, The Netherlands
(*correspondence: g.a.adnew@uu.nl)

²Centre for Isotope Research, Groningen University, The Netherlands

³Department of Meteorology and Air Quality, Wageningen University, The Netherlands

Precise measurement of the ^{17}O -excess in atmospheric CO_2 (expressed as $\Delta^{17}\text{O} = \ln(\delta^{17}\text{O}+1) - \lambda \ln(\delta^{18}\text{O}+1)$) allows to better constrain the exchange between atmosphere and biosphere/hydrosphere than using $\delta^{18}\text{O}$ alone, since $\Delta^{17}\text{O}$ is not directly dependent on $\delta^{18}\text{O}$ of soil and leaf water [1]. However, measurement of $\delta^{17}\text{O}$ of CO_2 with conventional isotope ratio mass spectrometers is challenging because of the isobaric interference of $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ on $^{12}\text{C}^{17}\text{O}^{16}\text{O}$. Conversely, $\delta^{13}\text{C}$ measurements need correction for the interference from ^{17}O . So far the techniques used to measure $\Delta^{17}\text{O}$ use either isotope equilibration or conversion of CO_2 to O_2 .

Using the new high-resolution gas-source isotope ratio mass spectrometer MAT 253 Ultra we developed a method to quantify $\delta^{17}\text{O}$ and $\delta^{13}\text{C}$ of CO_2 from the fragment ions $^{17}\text{O}^+$ and $^{13}\text{C}^+$ formed in the ion source. We present measurements of $\delta^{17}\text{O}$ and $\delta^{13}\text{C}$ of CO_2 and compare results using the fragment technique with the existing CO_2 - O_2 exchange method [2,3].

The fragment technique to measure $\delta^{17}\text{O}$ of CO_2 is simple and does not require chemical conversion. However, the ion current of the $^{17}\text{O}^+$ fragment is low and it requires long integration times to reach high precision

Measurement of $^{13}\text{C}^+$ directly is an alternative to deriving $\delta^{13}\text{C}$ from $\delta^{18}\text{CO}_2$, which does not require a ^{17}O correction. $\delta^{13}\text{C}$ measurement on the $^{13}\text{C}^+$ fragment is as precise as the measurement obtained from CO_2 molecule due to the relatively higher signal for the $^{13}\text{C}^+$ fragment. Isotope measurements on ion fragments may have many applications for other molecules, and may provide new insight into fractionation processes in a gas ion source IRMS.

[1] Hoag et al (2005) *Geophys.Res.Lett* **32**,1-5. [2] Mahata et al (2013) *ACS* **85**,6894-6901.[3] Barkan et al (2015) *Rapid Commun. Mass Spectrom* **29**,2219-2224.