

High precision isotope analysis of ^{17}O in CO_2 on oxygen ion fragments using the MAT 253 Ultra instrument

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Isotope ratio mass spectrometry (IRMS) measurements are traditionally carried out on the ionized target molecules, e.g. the $^{18}\text{O}/^{16}\text{O}$ ratio in CO_2 is determined from the single ionized $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ and $^{12}\text{C}^{16}\text{O}^{16}\text{O}$ ions at cardinal mass 46 and 44. Due to the limited mass resolution most IRMS systems cannot resolve isobaric interferences from other molecules (e.g. $^{14}\text{N}^{14}\text{N}^{18}\text{O}$) or from other isotopocules of the same molecule ($^{13}\text{C}^{16}\text{O}^{17}\text{O}$) and such interferences must be either eliminated by sample preparation procedures or accounted for by applying corrections. The issue is particularly critical when measuring the $^{17}\text{O}/^{16}\text{O}$ ratio in CO_2 because $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ cannot be mass resolved from $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ on common isotope ratio machines, even not with the high resolution instrument MAT 253 Ultra. As the abundance of the interfering molecule $^{13}\text{C}^{16}\text{O}^{16}\text{O}$ is about 15 times larger than the one of the target molecule $^{12}\text{C}^{16}\text{O}^{17}\text{O}$, so correction for the interference usually involves rather large errors. Therefore, high precision measurements of ^{17}O in CO_2 often involve chemical transformation or isotope exchange procedures, which can cause additional fractionation. Using the MAT 253 Ultra instrument we have developed isotope ratio measurements on O atom fragments of CO_2 . The oxygen isotopes can be clearly mass resolved from OH and H_2O and are collected interference-free at medium resolution. At an ion source pressure of about 2.5×10^{-7} mb, the signal intensities of the rare isotopes are about 300,000 cps for ^{17}O and 1,800,000 for ^{18}O . The precision achieved for the $^{17}\text{O}/^{16}\text{O}$ ratio is about a factor 1.5 worse than the counting statistics limit. The instrument is stable, thus precision continuously increases with measurement time. For very high precision measurements, the main limitation of the method is the long measurement time required; several hours of dual-inlet measurement are required to reach precisions for $\Delta^{17}\text{O}$ of about 20 per meg. The stable isotope ratio measurement on the O atom fragments is a new independent technique for measurement of ^{17}O in CO_2 that does not require any chemical processing. Atom fragment IRMS is applicable to many other molecules.