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High-Precision Triple Oxgyen Isotope Analysis of CO_2 by TILDAS

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High-precision ^{17}O measurements by IRMS are challenging because they require complicated sample preparation procedures, long measurement times, and relatively large samples sizes. Recently, tunable infrared laser direct absorption spectroscopy (TILDAS) has shown significant potential as an alternative technique for both clumped and triple oxygen isotope analysis of CO_2, although the ultimate level of reproducibility is unknown, partly because there are uncertainties about how TILDAS measurements should be related to an internationally accepted isotope abundance scale (e.g., VSMOW2-SLAP2, in the case of $^{18}O/^{16}O$ and $^{17}O/^{16}O$). We recently presented a method for high-precision triple oxygen isotope analysis of CO_2 by TILDAS, requiring ~8−9 μmol of CO_2 (or 0.9 mg carbonate) in 50 min, plus ~1.5 h for sample preparation and dilution of CO2 in N2 to a nominal 400 μmol mol−1 [1]. Using TILDAS, the overall reproducibility of $\Delta'^{17}O$ (CO_2) was 0.004‰ (4 per meg) for IAEA603 (*SE*, n = 6) and 10 per meg for NBS18 (*SE,* n = 4). Values corrected to the VSMOW2-SLAP2 scale are in good agreement with established techniques of high-precision IRMS, with the exception of $\Delta'^{17}O$ measured by platinum-catalyzed exchange of CO_2 with O_2. Compared to high-precision IRMS, TILDAS offers the advantage of 10 times less sample, and greater throughput, without loss of reproducibility. We show that careful and proper mixing of gas is critical when analyzing CO_2 in N_2 at trace concentrations. We also present a framework for correcting spectroscopic $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios to the VSMOW2-SLAP2 scale and show that overall reproducibilities from TILDAS can match those of IRMS methods. Furthermore, we show that minimising large instantaneous TILDAS electronics temperature changes is key to achieving high-precision measurements. The flexibility of the technique holds considerable potential for global biogeochemical monitoring, and applications to a range of geological materials. In particular, we are keen to explore the possibility of further standardisation and inter-laboratory comparison with other researchers employing TILDAS (or cognate optical techniques) for rare and multiply-substituted isotopologues of CO_2.

[1] Hare, Dyroff, Nelson & Yarian (2022) *Analytical Chemistry* 94(46), 16023-16032.