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High-accuracy measurements of N_2O concentration and isotopic composition of low and high concentration samples with small volume injections using Cavity Ring-Down Spectroscopy

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Nitrous oxide (N_2O) gas is among the major contributors to global warming and ozone depletion in stratosphere. Quantitative estimate of N_2O production in various pathways and N_2O fluxes across different reservoirs is the key to understanding the role of N_2O in the global change. To achieve this goal, accurate and concurrent measurement of both N_2O concentration ([N_2O]) and its associated isotopic ratios ($\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ & $\delta^{18}O$) is desired. Recent developments in Cavity Ring-Down Spectroscopy (CRDS) have enabled high-precision measurements of [N_2O] and Site-Preference-$\delta^{15}N$ (SP-$\delta^{15}N$) and $\delta^{18}O$ of a continuous gas flow. However, many N_2O samples are discrete with limited volume (<500 ml), and/or high [N_2O] ($>$ 2 ppm), and are not suitable for direct continuous measurements by CRDS. Here we present results of a small sample introduction and handling device, labelled as Small Sample Isotope Module (SSIM), coupled to and automatically coordinated with a Picarro isotopic N_2O CRDS analyzer to handle and measure high concentration and/or small volume samples. The SSIM requires 20 ml of sample volume per analysis at STP, and transfers the sample to the CRDS for high-precision concentration and isotope ratio measurements. When the injected sample is $<$ 20 ml at STP, a zero-air gas is optionally filled to make up the volume up to 20ml in the SSIM mixing chamber. We used the SSIM to dilute small volume (<20 ml) high [N_2O] samples and tested the effect of dilution on the measured SP-$\delta^{15}N$ and $\delta^{18}O$. In addition, we have implemented and tested a newly developed double injection method adequate for two, back-to-back, 20 ml sample injections. The basis of this method is the priming of the SSIM mixing chamber and the CRDS cavity with the first sample injection, then the second injection will have negligible dilution effect with the residual gas, and it can be accurately measured for both [N_2O] and isotopic ratio values. Results of these experiments indicate that [N_2O] can be accurately measured using the double injection method, while the single injection method tends to underestimate the [N_2O] by $\sim$20% and increase the isotopic memory effect from sample to sample. Our results also show that the precision of small sample injection into the SSIM-CRDS system, with careful injection technique, is identical to that of the continuous measurements using the CRDS alone, and that sample dilution of concentrated samples has minimal effect on SP-$\delta^{15}N$ and $\delta^{18}O$, as long as the [N_2O] is $>$300 ppb after dilution. Overall, the precision of SP-$\delta^{15}N$ measured using the SSIM is $<$ 0.5 ‰ and that of $\delta^{18}O$ is $<$ 1 ‰