High-accuracy Measurements of N_2O Concentration and Site-specific Nitrogen Isotopes in Small or High Concentration Samples

PICARRO

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Abstract

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 site-specific isotopic composition (SP-$\delta^{15}N$), namely $d^{15}N$-α and $d^{15}N$-β, is desired. Recent developments in Cavity Ring-Down Spectroscopy (CRDS) have enabled high precision measurements of [N_2O] and SP-$\delta^{15}N$ 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 measurements by CRDS.

Here we present results of a Small Sample Isotope Module 2 (SSIM2) which is 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 SSIM2 requires 20 ml of sample per analysis, and transfers the sample to the CRDS for high precision measurement. When the sample injection is < 20 ml, a zero gas is optionally filled to make up the volume. We used the SSIM2 to dilute high [N_2O] samples and <20 ml samples, and tested the effect of dilution on the measured SP-$\delta^{15}N$. In addition, we employed and tested a newly developed double injection method for samples adequate for two 20 ml injections. After the SSIM2 and the CRDS' cavity was primed with the first injection, the second injection, which has negligible dilution of the sample, can be accurately measured for both [N_2O] and SP-$d^{15}N$. Results of these experiments indicate that the precision of SSIM2-CRDS is similar to that of the continuous measurements using the CRDS alone, and that dilution has minimal effect on SP-$\delta^{15}N$, as along as the [N_2O] is >300 ppb after dilution. Overall, the precision of SP-$\delta^{15}N$ measured using the SSIM2 is < 0.5 ‰.

Instrument Set-up

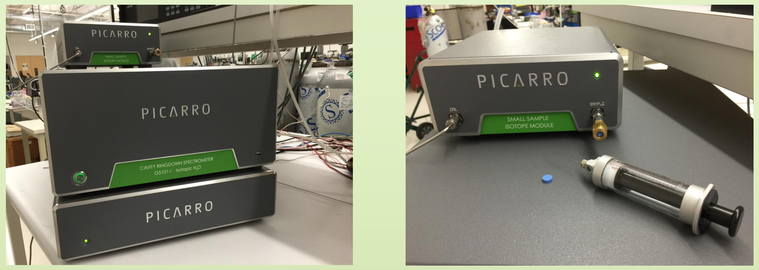

Figure 1. The set-up of an SSIM2-isotopic N_2O analyzer (left) and the detail of the syringe injection set-up for the single injection and dilution method. For the single and double injection method without out dilution, the sample port of the SSIM2 was connected directly to the gas cylinder.

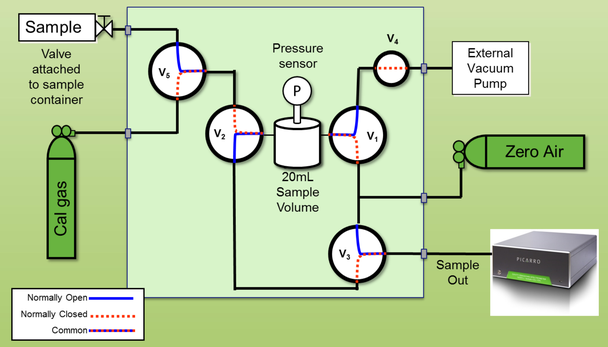

Figure 2. The schematics of the SSIM2. The SSIM2 is a 5 valve peripheral that depends on the use of a closed chamber to hold a sample throughout the analysis. Long averaging times are achieved with relatively small samples by allowing the analyzer to pull on the closed volume. The instrument's flow is controlled by an outlet valve, which closes as the sample is drawn in, until the SSIM2 chamber pressure equilibrates with the cavity pressure set-point. At this stage it is possible for the instrument to measure the small sample continuously until the optimal precision is reached. Between samples, the chamber is cleaned by alternating vacuum evacuation and purging with zero air (ZA).

Results of Single and Double Injection Methods

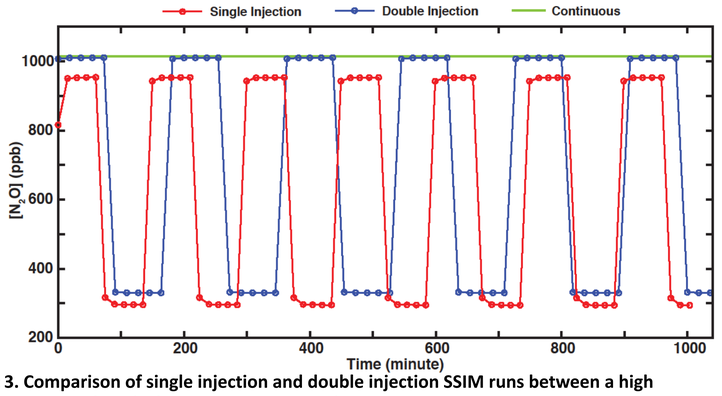

Figure 3. Comparison of single injection and double injection SSIM runs between a high concentration tank and a low concentration tank.

Gas samples from a 300ppb and a 1000ppb N_2O gas cylinder were run alternately through the SSIM for >16 hours using the singe injection (red) and double injection (blue) methods. At each concentration level, the sample was run for 5 times. Compared with the single injection method, double injection has lower throughput (~3 samples/hour compared to ~4 samples/hour for single injection). However, it has more accurate concentration results while the single injection method gives measurements that are <95% of the true concentration. More importantly, double injection reduces the tank-to-tank memory that can be seen in the difference between the first replicate and the second.

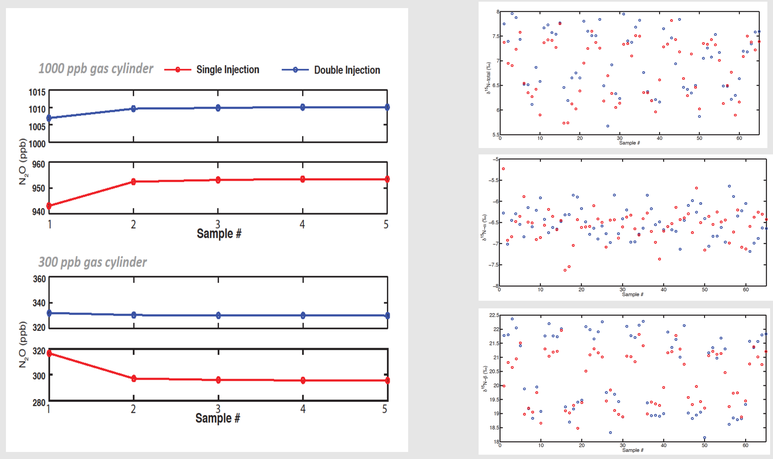

Figure 4. Close up inspection of 5 replicates of double injections vs. 5 replicates of single injections (left), and results of the isotope measurements (right).

Not only does the single injection yield a less accurate concentration result, but the first replicate is noticeably contaminated with the remnants of the previous tank. This is due to the inherent dilution of the first injection. Before a sample is loaded into the SSIM, the SSIM chamber is cleaned out with ZA, and then pumped down by a vacuum. Approximately 2-10 torr of gas will remain in the SSIM chamber before a sample is injected. This small remaining volume of gas, while composed mostly of clean ZA, can also contain minor remnants of the previous sample. Regardless, this volume of gas will mix with the new sample when it is introduced to the chamber, thus diluting the sample and introducing errors to the isotopic measurements.. The double injection method allows the analyzer to 'sip' on the first injection for some time until the SSIM chamber has been mostly equilibrated with the cavity pressure and the outlet valve has closed. Then, the same sample is reintroduced to the SSIM chamber for a second time. This allows the second injection to mix with the remnants of the first, which significantly lessens the dilution with ZA and the contamination with the previous sample, resulting in reduced memory and more accurate concentration (and isotopic) measurements. Plots of the various isotopic measurements taken from both double injection and single injection SSIM sampling show no significant difference in the sample to sample precision. There are also no visible memory affects, but that is likely because the two tanks are similar with respect to isotopic composition.

Results of Syringe Injection Coupled with Dilution of High Concentration Samples

Injections of various volume (~5-20ml) of gas from a 1000 ppb N_2O cylinder were used to test the effect of dilution when running samples with volume <20 ml. The results are shown in Figure 5. Injections in red were performed by Kuan, while injections in blue were performed by Melissa. Concentration decreases linearly as you decrease the volume injected (5a). Overall, it is important to note the varying size of the error bars in all of the plots, which indicate the repeatability of the replicate injections at each volume, due to the individual methods of the syringe operator.

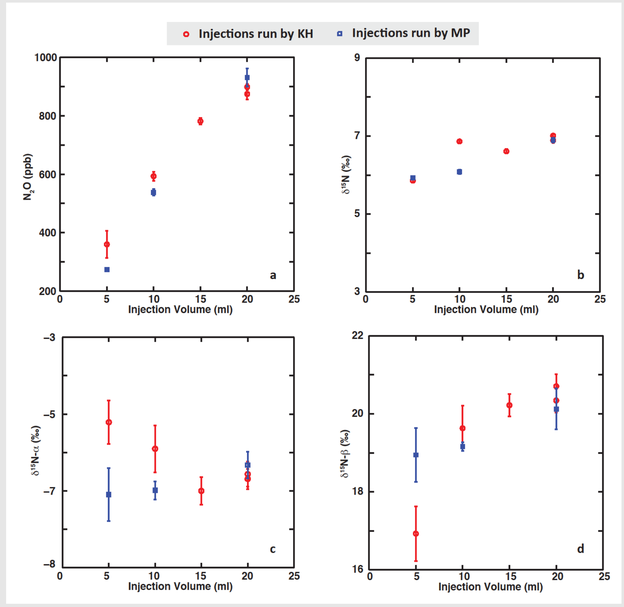

Figure 5. Results of concentration and isotope measurements using the single injection and dilution method. Five duplicates were run at each injection volume.

Figures 5b-d show the injected volume prior to dilution vs. the post dilution values of the total $\delta^{15}N$, $\delta^{15}N$-α, and $\delta^{15}N$-β. The precision of the replicates at each volume, indicated by the error bars, remain within the guaranteed precision of the instrument, but tend to worsen with lower injection volumes. There was up to a 3 per mil difference in the measured isotopic compositions at different injection volumes. While part of the difference could be due to a spectroscopic dependence of isotope measurements on the N_2O concentration, the major source of errors might be attributed to leaking and contamination of room air during the injections. The human errors associated with the manual injections are strongly dependent on the methods of one person to the next, e.g. Melissa's runs showed significantly smaller isotopic change throughout the volume range (within 1.5 per mil).

Conclusions and Recommendations

Regarding the adoption of the double injection technique, the first barrier to entry is sample volume. In order to even consider the method, each replicate requires ~40mL of sample. If that requirement is met, overall double injection is the winning method. While it does need 3 extra minutes of cycle time (therefore lowering sample throughput), it increases concentration accuracy and reduces sample-to-sample memory. Consequently, relative to single injection, the first replicate is significantly more useful in analysis.

Regarding syringe injection and the dilution of high concentration samples, overall the method shows merit and the precision of the isotopic measurements over a variety of injection volumes is well within the expected performance of the instrument on its own. A potential risk is the introduction of human error and technique biases at smaller injection volumes. Careful adherence to a validated injection method is advised, especially at injection volumes less than 10mL. Minor variations in timing, possible atmospheric contamination, and the precision to which the syringe is filled to the desired volume all result in inconsistencies from injection to injection.