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## PURPOSE

•There are numerous compounds in atmosphere that are important for the NO<sub>x</sub> and HO<sub>x</sub> cycle, O<sub>3</sub> formation, and aerosol growth (e.g., isoprene, α-pinene, oxidants of these compounds); however, there are no commercial gas cylinder standards for these compounds.

•Currently, there are two cited methods to make cylinders: gravimetric [1-2, 5-9] or volumetric [3-4]. Both methods introduce uncertainty in the concentration of the analyte(s) due to the way the analyte(s) are prepared or injected into the cylinder.

•**GOAL:** To develop a new method to prepare a standard (in μmol/mol or ppm range) gas cylinder with at least 0.3% (one standard deviation) uncertainty for the laboratory to use in the future.

## METHOD DEVELOPMENT

•Pull an aliquot of CH<sub>2</sub>Cl<sub>2</sub> (99.9% Purity) into micro-syringe and weighed on analytical balance.



•Flow ~3 L/min high purity N<sub>2</sub> through glass-T into standard gas cylinder (Figure 1). Inject CH<sub>2</sub>Cl<sub>2</sub> into glass-T after ~5 minutes of flow. Re-weigh micro-syringe after injection.

•After ~20 minutes, directly connect N<sub>2</sub> tank to standard gas cylinder (Figure 2). Fill until approximate pressure equilibrium.

•Rolled cylinders to ensure CH<sub>2</sub>Cl<sub>2</sub> is well mixed throughout entire cylinder.

•Sampled cylinder with Shimadzu GC-14B with <sup>63</sup>Ni Electron Capture Detector (Figure 3).

•Two columns used: between March and July, a Supel-Q PLOT Column (Column 1, 30 m x 0.32 mm) and after August, a Rtx-1701 Column (Column 2, 30 m x 0.53 mm).



FIGURE 2. Direct flow set-up.

•The columns were held isothermally.

•The sample loop was ~0.62-mL.

•A vent between the standard gas cylinder and the 6-port valve was used to ensure build of pressure did not occur in the instrument.



FIGURE 3. GC-ECD Set-up.

## RESULTS

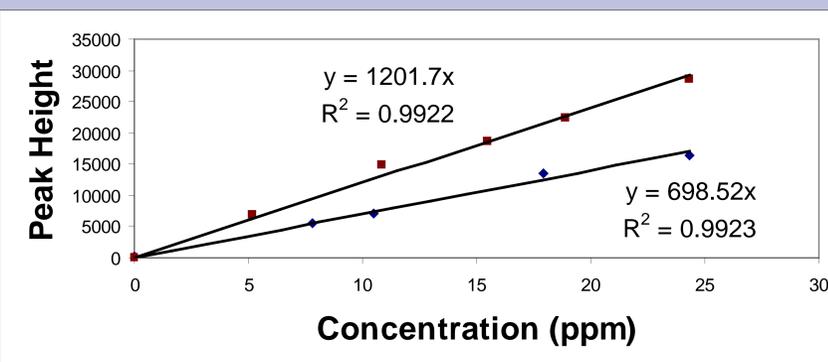


FIGURE 4. Example calibration curves for CH<sub>2</sub>Cl<sub>2</sub> on both columns. The top calibration curve is for Column 1 and the bottom calibration curve is for Column 2. Note: error bars are less than ±200 counts peak height.

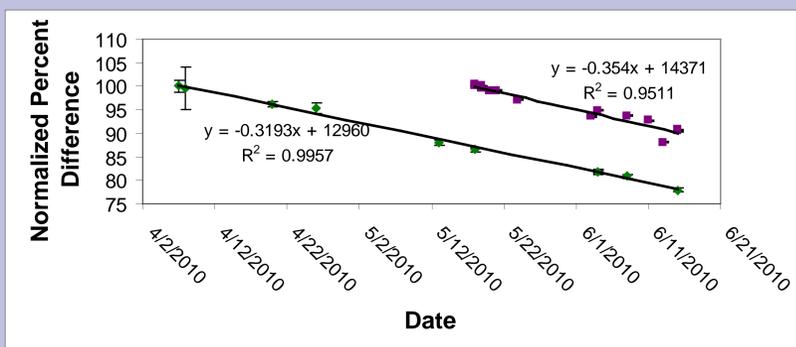


FIGURE 5. Change in analyte concentration from cylinder fill to September. Cylinder 2 is green and Cylinder 1 is purple. Error bars are at 95% confidence interval.

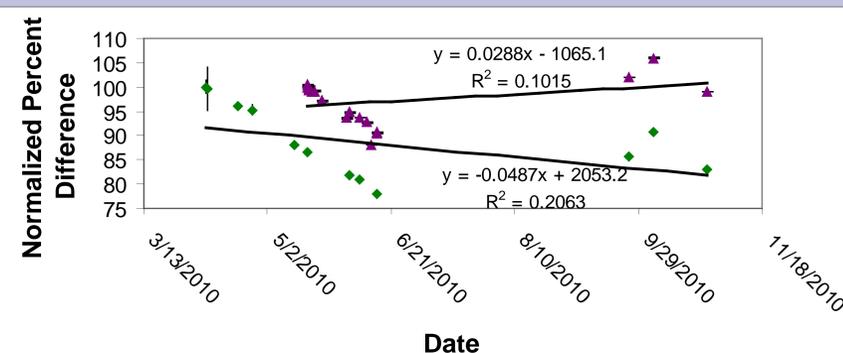


FIGURE 5. Change of concentration from initially making cylinders to present. Error bars are at 95% confidence interval.

TABLE 1. Calculated and measured concentrations. Numbers in parentheses are one standard deviation.

	Calculated Concentration	Measured Concentration	% Difference
Small Concentration Cylinder (Cylinder 1)	6.17 (±0.04) μmol/mol	7.5 (±0.3) μmol/mol	22%
Large Concentration Cylinder (Cylinder 2)	11.5 (±0.0) μmol/mol	22.4 (±1.9) μmol/mol	95%

## DISCUSSION

•Both slopes in Figures 5 and 6 are statistically different from 0.

•Before September, the decrease of concentration was nearly linear. After September, cylinder 2 is at approximately 87% of its original value and cylinder 1 is at approximately 102% of its original value.

•The decrease in concentration is not fully understood. It is possible that the cylinders are not well-mixed; however, this would then yield results that are low. Similarly, losses of the analyte during the injection process, or during sampling from the cylinder would yield results that are low.

•There was a larger change of concentration over time and percent difference in calculated versus measured than literature [1-9]; however, in those references, most of the analytes are hydrocarbons instead of halogenated organic compound. Also, the cylinders were analyzed over longer time periods (~2 years minimum), which could result in a more stable average (Figure 4 versus Figure 5).

•The percent difference between calculated and measured concentrations is unclear. Contamination from the glass-T and transfer lines were tested and found to be negligible. Also, the analytical balances were carefully calibrated.

•There is a 4% and 8% (1 standard deviation) uncertainty with cylinders 1 and 2, respectively. This corresponds well with G. C. Rhoderick's [7] results; however, lower than the theoretical percent uncertainty from propagation of error from balances (~0.3%).

## FUTURE WORK

•We are working to understand the difference in the calculated and observed concentrations. Future tests will include trying multiple approaches in parallel and trying different polarity compounds.

•This work is necessary in order to accurately calibrate instruments to measure low concentrations species in the atmosphere. The drifts currently observed would cause an over estimation of the gases.

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## ACKNOWLEDGMENTS

- I would like to acknowledge the Shepson group for their support during this project.
- I would also like to acknowledge NSF for funding for the project.